

Z. JAWOROWSKI, T. V. SEGALSTAD & V. HISDAL

ATMOSPHERIC CO₂ AND GLOBAL WARMING:

A CRITICAL REVIEW SECOND REVISED EDITION



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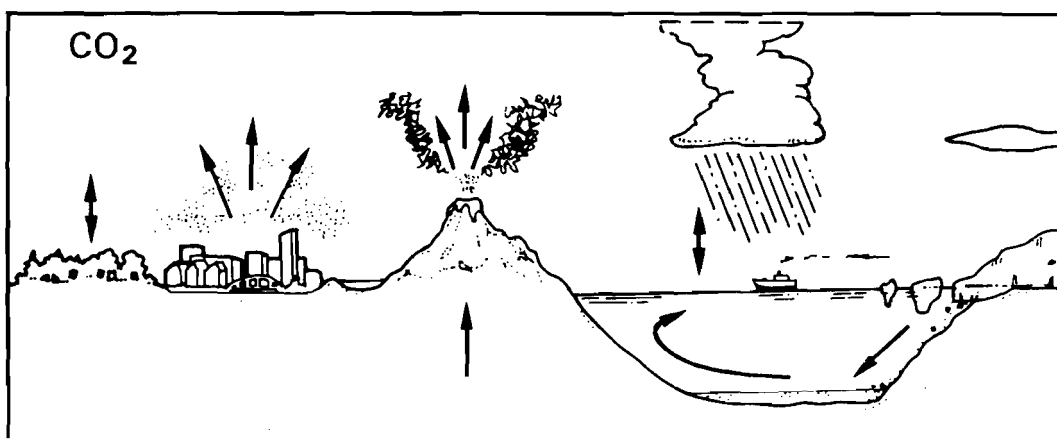


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**Atmospheric CO₂ and global warming:
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NORSK POLARINSTITUTT
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PREFACE TO SECOND EDITION

The supply of the first edition of this work (Norsk Polarinstitutt Rapportserie Nr. 59, 1990) was exhausted by the end of 1991. In this second edition we review new publications available to us since publication of the first edition. We have also taken into account some of the comments and critical suggestions made by readers.

Feedback from our readers has indicated that we addressed a controversial issue. Various aspects of the "greenhouse" warming hypothesis have been criticized before, but to our knowledge, our report is the first critical review of the CO₂ studies in glaciers.

The glacier CO₂ data are often interpreted as representing the composition of the pre-industrial atmosphere, and they are important input parameters in climate change calculations. The verification of the reliability of the glacier data is therefore of fundamental importance for validation of the hypothesis on a global warming caused by human activities.

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Oslo, April 1992

SUMMARY

The projections of man-made climate change through burning of fossil carbon fuels (coal, gas, oil) to CO₂ gas are based mainly on interpretations of measured CO₂ concentrations in the atmosphere and in glacier ice. These measurements and interpretations are subject to serious uncertainties.

Dominant factors in the Earth's surface CO₂ cycle are the ocean, in addition to mineral equilibria. Due to their vast buffer capacity, they stabilize the geochemical equilibrium of CO₂ gas between the hydro-, atmo-, litho- and biosphere. Radiocarbon (¹⁴C) studies indicate that the turnover time of dissolved organic carbon in the upper ocean is a few decades. This suggests that CO₂ produced by burning the Earth's whole fossil carbon fuel reservoir would be dissolved in the ocean before reaching the double concentration of its current atmospheric level.

The 19th century measurements of CO₂ in the atmosphere were carried out with an error of up to 100%. A value of 290 ppmv (parts per million, by volume) was chosen as an average for the 19th century atmosphere, by rejecting "not representative" measured values which differed more than 10% from the "general average for the time". This introduced a subjective factor in the estimates of the pre-industrial level of CO₂ in the atmosphere.

The Mauna Loa (Hawaii) observatory has been regarded an ideal site for global CO₂ monitoring. However, it is located near the top of an active volcano, which has, on average, one eruption every three and a half years. There are permanent CO₂ emissions from a rift zone situated only 4 km from the observatory, and the largest active volcanic crater in the world is only 27 km from the observatory. These special site characteristics have made "editing" of the results an established procedure, which may introduce a subjective bias in the estimates of the "true" values. A similar procedure is used at other CO₂-observatories. There are also problems connected to the instrumental methods for measurements of atmospheric CO₂.

The CO₂ concentrations in air bubbles trapped in glacier ice are often interpreted as previous atmospheric concentrations, assuming that the composition of the air in the bubbles remained unchanged. This was based on another assumption: liquid does not exist in ice below a mean annual temperature of about –24°C, and no changes due to diffusion may be expected. However, it was recently found that liquid can be present in Antarctic ice at temperatures as low as –73°C. Numerous studies indicate that, due to various chemical and physical processes, the CO₂ content in ice can be largely enriched or depleted in comparison with the original atmospheric level. In the air inclusions from pre-industrial ice the CO₂ concentrations were found to range between 135 and 500 ppmv.

Methods using dry extraction of CO₂ from crushed ice release only about half of this gas present in the ice. CO₂ in air inclusions can penetrate the ice by diffusion or dissolution into the liquid present at the ice grain boundaries, at a rate different from rates of other gases in the air. A problem for the determination of CO₂ levels in gas inclusions is the formation of solid CO₂ clathrates (hydrates). Other gases in air also form clathrates, but at different temperatures and pressures. This leads to important changes in the

composition of the inclusion air at different core depths and indicates that glacier ice cannot be regarded as a steady state matrix suitable for observation of long-term atmospheric trends. Thus, the results of CO₂ determinations in air inclusions in ice cannot be accepted as representing the original atmospheric composition.

Another difficulty in this respect is a speculative assumption that air is 90 to 2800 years younger than the ice in which it is trapped. Without this assumption the CO₂ concentration in air recovered from 19th century ice is the same as now. Atmospheric N₂/O₂/Ar ratios in trapped air are not preserved. Instead the ratios agree with those from aqueous solubility data. ⁸¹Kr and ³⁹Ar measurements indicate that 36 to 100% of gas from the ice cores are contaminated by ambient air.

Paleo-temperature calculations based on light stable isotope ratios (D/H and ¹⁸O/¹⁶O) in ice have large uncertainties. After the discovery of liquids between ice crystals in the deeply frozen Antarctic ice, considerable isotopic exchange and fractionation should be expected in the ice, making calculated paleo-temperatures meaningless if phase changes occurred in the presence of a mobile fluid phase.

Attempts have been made to calculate the paleoatmospheric CO₂ content from ¹³C/¹²C carbon stable-isotope ratios in tree rings. It is concluded here that the CO₂ content in the atmosphere calculated from such carbon isotope analyses cannot be considered a valid tool in paleoclimatology, nor can it be used as evidence of changing atmospheric CO₂ levels.

The so-called increasing "greenhouse effect" signal, i.e. anthropogenic increase of the global air temperature, which was claimed to have been observed during the last decades, is not confirmed by recent studies of long temperature series.

In the Arctic, according to model calculations, this warming should be most pronounced. However, cooling rather than warming has been recorded in this region during the last two decades. Glacier balance studies provide evidence for a recent decrease in glacier retreat, and for an increased accumulation over the polar ice caps, corresponding to a sea level lowering of about 1 mm per year.

1. INTRODUCTION

Only about half the incoming solar energy is absorbed by the Earth's surface. The rest is scattered back and to some extent absorbed by the atmosphere (clouds included), or reflected by the ground. The Earth itself radiates at wavelengths much longer than those of solar radiation. This Earth radiation, unlike the solar radiation, is strongly absorbed in the atmosphere. The absorption is mainly caused by water vapor and clouds, but also by some trace gases. Only a very small part of the radiation emitted by the ground escapes directly to space. In this way the atmosphere is heated, and returns radiative energy to the Earth's surface, where it is again absorbed and re-radiated. Thus a remarkable exchange of thermal energy takes place between the ground and the lower atmosphere. These processes, somewhat misleadingly called the "greenhouse" effect, are responsible for the relatively high mean surface temperature on the Earth, of about 14°C. If the Earth had no atmosphere the corresponding temperature would be about –18°C.

The term "greenhouse effect" is now often used to name a predicted increase in the temperature of the lower atmosphere as a consequence of man's release of CO₂ and other trace gases to the atmosphere. This predicted additional effect will in the following be referred to as an *increasing* "greenhouse effect" or "greenhouse" *warming*.

In the Earth's atmosphere dry air consists of nearly 78% (by volume) nitrogen (N₂), about 21% oxygen (O₂) and about 1% argon (Ar). In humid air the water vapor content varies from about 3% in the tropics to a small fraction of this quantity in the polar regions. Carbon dioxide (CO₂) is just a trace component, with a concentration of about 0.035% (= 350 ppm), but it plays an important part in plant and animal life processes. The concentration of CO₂ varies with time and place. It has been found, for example, that the concentration may double during one single day over a wheat field (Fergusson, 1985).

During the 1970s and the first half of the 1980s several climatic model computations predicted that for a hypothetical doubling of the average atmospheric CO₂ concentration during the next 60 years, the average global temperature will increase by 1 to 5°C (see e.g. review by Braathen et al., 1989), that the polar regions will warm more than the lower latitudes, up to 8 to 10°C (Schneider, 1975; Manabe and Wetherald, 1980), and that the seasonal variations will be greatest in the north polar regions (Ramanathan et al., 1979). These models also predicted considerable changes in the geographical distribution of precipitation. At the end of the 1980s more sophisticated models revised the earlier predictions substantially, decreasing the net impact on the climate and changing its geographical distribution. A recent study estimated a 1.2°C increase in the surface and tropospheric temperature due to doubling the atmospheric CO₂ (Lorius et al., 1990), assuming no feedback processes.

To the present natural global atmospheric flow of CO₂, man's burning of fossil carbon may add somewhere between 0.1 and 3.6%, according to different estimates. CO₂ is one of about 40 trace "greenhouse gases" present in the atmosphere (Ramanathan et al., 1985). Water vapor contributes the most to the total "greenhouse effect" of the atmosphere of about 150 W/m² (Raval and Ramanathan, 1989). According

to Kondratyev (1988) H₂O contributes about 62%, CO₂ 21.7%, O₃ 7.2%, N₂O 4.2%, CH₄ 2.4%, and other gases 2.4% to the mean "greenhouse effect" of the atmosphere.

A doubling of CO₂ would increase its "greenhouse" contribution to about ~4 W/m² (Raval and Ramanathan, 1989 a). Landsberg (1974) estimated that only 3% decrease in atmospheric water vapor, and a 1% increase in cloudiness can compensate the warming from an anticipated CO₂ doubling (other conditions held constant). As a whole, the influence of clouds on atmospheric temperature is still an unsolved problem (e.g. Schlesinger and Mitchell, 1987). The predictions of CO₂ doubling are based on an assumption that all past human activities have contributed about 21% of the current atmospheric CO₂, the level of which is supposed to be 25% higher than in the pre-industrial period (IPCC, 1990). This assumption is based on glacier studies. As will be seen later on these studies do not provide a reliable basis for such an estimate.

The level of atmospheric CO₂ depends on constantly changing thermodynamic equilibria between its sources and sinks. Oceanic flows of this gas in and out of the global atmosphere are important for the CO₂ budget. Even very small natural fluctuations of these oceanic flows can mask the man-made CO₂ inputs into the global atmosphere.

Several studies have suggested that radiative heating of 4 W/m² caused by the doubling of atmospheric CO₂ would lead to a global warming of 3.5 to 5°C (Hansen et al., 1984; Wilson and Mitchell, 1987; Washington and Meehl, 1984; Wetherald and Manabe, 1988). The total present global mean warming due to all trace "greenhouse" gases added by man of about 2 W/m², is below the estimated natural variation of about ± 5 to 10 W/m² in the global net radiation (Raval and Ramanathan, 1989). The positive (warming) forcing by clouds is about 30 W/m² (Raval and Ramanathan, 1989). This "greenhouse effect" of clouds is approximately fifteen times larger than that resulting from a hypothetical doubling of CO₂ (increase from ~2 to 4 W/m²). A new estimate of Ramanathan et al. (1989 b) suggests that "the CO₂ concentration in the atmosphere has to be increased more than two orders of magnitude to produce a "greenhouse effect" comparable to that of clouds". The negative cloud forcing (due to a high albedo at the upper cloud surface) is about –50 W/m². From such figures one gets a net cloud forcing of about –20 W/m² (30 minus 50), i.e. much higher than the claimed man-made positive forcing of CO₂ doubling.

Ramanathan et al. (1989 b) demonstrated that the clouds have a large net cooling effect on the Earth, which will offset the possible increasing "greenhouse effect" warming. This is because an increase in the global temperature will increase the amount of clouds in the troposphere, introducing a strong negative radiative feedback. It is claimed that the total past anthropogenic "greenhouse" forcing (due to CO₂ and other trace gases) between 1850 and 1985 should cause a global surface warming of 0.8 to 2.4°C (Ramanathan et al., 1989 b). However, no such warming has been observed, which may indicate that the estimate of the "greenhouse gases" increase is incorrect or that the negative cloud forcing of about –20 W/m² (or some other negative forcings) is sufficiently large to stabilize the increasing "greenhouse effect" warming. This latter supposition was confirmed by Slingo (1989) who found that the radiative forcing by doubled CO₂ concentrations can be balanced by modest increases in the amount of low clouds.

Wigley et al. (1989) revived the idea posed by Mitchell (1975) that SO_2 -derived cooling may offset considerably the "greenhouse" warming. SO_2 originates from dimethylsulfide from the oceans (Charlson et al., 1987), volcanic emissions, and from man-made sources. The cooling effect is partly due to the absorption of incoming solar radiation by sulfuric acid in the stratosphere and partly due to an increase of cloud condensation nuclei in the atmosphere. The latter effect is due to H_2SO_4 and sea-salt aerosols (Latham and Smith, 1990) and serves to "brighten" clouds (increase their albedo), thereby reflecting part of the incoming solar radiation back into space. Satellite data now confirm that the stratocumulus clouds (one of the most common cloud types on Earth, and the variety most likely to be affected by an increasing number of condensation nuclei) are indeed considerably brighter in the lee of regions of major anthropogenerated SO_2 emissions (Cess, 1989).

Wigley (1989) argued that man-made SO_2 is sufficiently large to offset significantly the global warming that might result from the "greenhouse effect", and to cool the Northern Hemisphere relative to the Southern Hemisphere, because most of the man-made SO_2 emissions occur in the Northern Hemisphere. Wigley (1989) supposed that the man-made SO_2 -derived (negative) forcing might explain the inconsistency between General Circulation Model (GCM) predictions of current warming and observations. To substantiate this Wigley cited two sulfate records from ice cores collected in southern Greenland showing up to three-fold increase during the twentieth century. The temperature in this region is high enough to allow summer melting, which may lead to changes in chemical composition of snow and ice (Jaworowski et al., 1992). However, seven other studies in the Arctic and five studies in Antarctica demonstrated no increase of sulfate or acidity in snow and ice during the past century. These studies indicate that there were covariations of the sulfate content in precipitation from the Southern and Northern Hemisphere in relation to major volcanic events, and that during the last decades the concentration of sulfate in precipitation in the Arctic was similar to that in Antarctica (Jaworowski, 1989). Thus Wigley's hypothesis is not substantiated.

A main feature of the predictions of almost all climate models is a relatively large warming at high latitudes. Therefore polar regions may be assumed to be the most promising ones for detection of any current increasing "greenhouse effect" warming. Temperature and to some degree glacier records can be used to check these model predictions. A discussion of computer modelling with the help of GCM is, however, beyond the scope of this report. Cess et al. (1989) compared 14 different models of this kind and showed that from the same input data the models produced results which varied greatly, i.e., both cooling and warming of the climate. Also in Cess et al. (1991) the net effect of snow feedback produced by 17 models differed markedly, ranging from cooling to warming. In this latter paper it was demonstrated that the conventional explanation that a warmer Earth will have less snow cover, resulting in a darker planet, absorbing more solar radiation, is overly simplistic.

If the present GCM modeling is fit for predicting future climate, it should also reproduce the past climates. However, according to Street-Perrott's (1991) analysis of such modeling, this point is still not reached. The ocean is a dominating factor in determining the Earth's climate. However, in these models the enormous

heat capacity of the ocean water mass and the oceanic currents are still not taken into account in a satisfactory way (Moene, 1991).

As will be seen from the discussion below, the hypothesis of an imminent climatic change is based on data subject to serious uncertainties and inconsistencies. These uncertainties should be factored into policy decisions in view of the staggering costs of implementation of "anti-greenhouse" decisions on a global scale. In the United States alone these costs may reach 3.6 trillion US dollars (Passel, 1989). Implementation of the CO₂ tax of 500 US dollars per metric ton of carbon would increase the price of crude oil about 3.7 times (to more than 60 dollars per barrel) and of utility coal about 8.3 times (to more than 276 dollars per short ton) (Anonymous, 1992). This might have serious negative social consequences both for developed and third world countries reaching beyond the 21st century. Such consequences should be weighed against the very uncertain predictions of environmental effects of an increase in atmospheric CO₂.

In most cases scientists are aware of the weak points of their basic assumptions and simplifications needed to interpret the results of measurements or to create models. However, these uncertainties are mostly ignored or banished to a subordinate clause when the results are presented by politicians or mass media. In the process of forming environmental policy the preliminary hypotheses are transformed into "reliable facts" when presented to the public. The magnitude of "normal" natural reservoirs, fluxes, and variations are not presented and not compared to claimed "abnormal" anthropogenic contributions. A more balanced view is certainly needed.

The most important basis of the hypothesis of man-made climatic warming due to burning of fossil carbon fuels are the measurements of CO₂ in air and in glacier ice, hydrogen and oxygen isotopes in glacier ice, carbon isotopes in tree rings, and 100–150 years long atmospheric temperature records. In this paper we critically review these measurements and their interpretations, in order to test the nowadays widely accepted postulate that "the change in atmospheric CO₂ is not just a fluctuation of nature, but is predominantly the consequence of the activities of mankind – chiefly the burning of fossil fuels such as coal, gas and oil" (Rowland and Isaksen, 1988). We also compare the quantities of anthropogenic contributions with known fluxes of natural reservoirs, and discuss air temperature and glacier balance records, which should reveal signals of an increasing "greenhouse effect".

2. THE CO₂ BUDGET

2.1 CO₂ FLOWS AND RESERVOIRS

Most of the recent attempts at predicting an increasing "greenhouse effect" have assumed a doubling of the present atmospheric CO₂ level, which is about 350 ppm, due to fossil fuel burning during the next 30 – 60 years. To estimate the reliability of this basic assumption, the size of the various sources and sinks of atmospheric CO₂ should be taken into account.

It is usually accepted that fossil carbon fuel burning contributes about 5 GT C (carbon equivalents in Gigatonnes = 10¹⁵ g) per year, i.e. about 3.6% of the global natural CO₂ flux of 169 GT C per year (Lansitt and Niehaus, 1989). However, Fergusson (1985) estimated the man-made contribution to be only about 0.1%. Fluctuations in the natural flux of CO₂ (Table 1) are generally higher than this man-made contribution.

The yearly CO₂ exchange between atmosphere and ocean, and between atmosphere and biosphere amounts to about 23% of the estimated pre-industrial atmospheric CO₂ content. In contrast, the present annual man-made input due to fossil fuels amounts to 0.8% of atmospheric CO₂ (Oeschger and Siegenthaler, 1988). This means that a small fluctuation in the natural exchange rate would mask the fossil fuel contribution.

If all fossil fuel resources (approximately 7000 GT C) were burned immediately, the current atmospheric content of CO₂ (about 700 GT C) would suddenly increase by a factor of 11, and would then dissolve in the ocean and be precipitated as carbonates in the bottom deposits (Walker and Drever, 1988). Such an assumption is, of course, rather unrealistic, as the CO₂ residence time in the atmosphere is only about 5 years (Bolin and Keeling, 1963; Stumm and Morgan, 1970; Broecker and Peng, 1974; Sundquist, 1985), and as the existing resources are supposed to be exhausted in approximately 300 years. According to Gorshkov (1982) the ocean is so powerful a sink for CO₂ that after burning all existing fossil fuels, the CO₂ contribution to the atmosphere can not increase by more than 35–40%.

CO₂ consumed annually by the photosynthesis of land plants give fluxes in the range 10 – 70 times higher than produced by man; photosynthesis by marine plants give fluxes in the range 50 to 250 times higher (Revelle and Suess, 1957). Such large natural sources and sinks would most likely mask the effect of fossil carbon fuel burning, which accounts for just a tiny fraction of the global atmospheric flux of this gas. Just small fluctuations in the dissolved marine carbon reservoir (38,000 GT C; Bolin, 1989), the sedimentary carbonate carbon reservoir (60,000,000 GT C; Walker and Drever, 1988), the vast carbon reservoir of the Earth's interior (constantly being tapped by volcanic activity), or short-term fluctuations such as due to the El Niño – Southern Oscillation (ENSO) phenomenon occurring every few years (about 2 GT C per event; Gaudry et al., 1987), would probably obscure the fossil fuel contribution of about 5 GT C per year.

As recently found in a modelling computation, for simulations run with twice the present-day CO₂ levels, strong negative feedbacks appear due to carbon storage in terrestrial biota and soils (Prentice and Fung, 1990). These negative feedbacks remove 235 GT of carbon from the atmosphere. From a carbon cycle

Table 1. Current reservoirs of carbon at the Earth's surface and annual fluxes of CO₂ (expressed as carbon equivalents in Gigatonnes = 10¹⁵ g) into the atmosphere.

	GT of carbon	References
RESERVOIRS		
Sediments ¹	60,000,000	Walker and Drever, 1988
Marine dissolved organics	1,000	Bolin, 1989
Marine dissolved inorganics	38,000	Bolin, 1989
Fossil fuels (exploitable)	7,200	Walker and Drever, 1988
Atmosphere	727	Rose et al., 1983
Soil	1,300	Prentice et al., 1990
Terrestrial biomass	834	Prentice et al., 1990
Marine biomass ²	42	
ANNUAL FLUXES		
		mansiti et al., 1989
NATURAL		
Ocean	106	
Land	63	
TOTAL	169	
MAN-MADE		
Fossil fuels and land use	6	

¹ Near surface

² Calculated from a total mass of marine biota of 10¹⁸ g (Nriagu, 1978) and from carbon concentration in these biota assumed to be 0.04 gram carbon per gram wet weight (GESAMP, 1983).

model it was estimated that the marine reservoir contains, in the form of dissolved carbonic acid, at least 37% of the fossil fuel CO₂ produced in the past (Broecker et al., 1979). If the same fraction were assumed for the future releases, it would correspond to about 87 GT C. The terrestrial biota, soils, and marine inorganic carbon sinks would then be large enough to remove 322 GT of carbon from the atmosphere. This is more than enough to remove the anthropogenic amount introduced into the atmosphere during the next 50 years, at the current consumption rate of fossil fuels.

The enormous sink of marine biota and of marine dissolved organics is not accounted for in the current models of the global carbon cycle (e.g. Oeschger et al., 1975; Siegenthaler and Oeschger, 1987). Therefore such carbon cycle models should be regarded as incomplete.

The CO₂ content in the atmosphere is dependent on the natural climatic changes through modulation of the ocean upwelling in low latitudes. An intensified upwelling of deep water rich in calcium, phosphorous, potassium, and other biogenic components rises the rate of formation of calcium carbonate and reduces the transport of CO₂ from the ocean to the atmosphere. Thus the atmospheric CO₂ content may be controlled by the climate (Kondratyev, 1988). Cooling and warming of ocean water will also influence the CO₂ flux. According to Takahashi (1961) heating of sea water by 1°C will increase the partial pressure of atmospheric CO₂ by 12.5 ppm during upwelling of deep water. For example the 12°C warming of the Benguela Current should increase the CO₂ partial pressure by 150 ppm. In reality some of this CO₂ is precipitating as CaCO₃.

The rise of biogenic Ca²⁺ and expulsion of CO₂ from upwelling of relatively warm water will increase the thermodynamic activities of Ca²⁺ and CO₂, and facilitate precipitation of calcium carbonate. This precipitation is not complete, so the atmospheric CO₂ will rise (see next section), as observed by Takahashi (1961).

2.2 CO₂ EQUILIBRIA

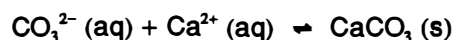
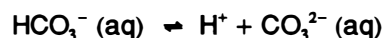
Table 1 shows that the ocean is the dominant factor in the CO₂ cycle of the Earth's surface. Therefore, we discuss briefly the geochemical equilibria that govern the relationship between atmospheric and oceanic CO₂. The inorganic part of the CO₂ cycle in the atmosphere/hydrosphere/lithosphere system is buffered with respect to pH by carbonate equilibria (see below). The salinity of the ocean is held constant by erosional and depositional processes and by mineral equilibria. All parts of the system, including CO₂ in the atmosphere, are therefore thermodynamically buffered and will tend to establish a chemical equilibrium at a given temperature. For a change in temperature, new chemical equilibria apply, and a new value for the partial pressure of CO₂ will be established (Rubey, 1951; MacIntyre, 1970). It appears from the work by Smith and Jones (1985) that wind is capable of pumping CO₂ into the water, thereby establishing an increased partial pressure of CO₂ in the surface water. This is due to pressurization of bubbles generated by breaking waves.

The oceans to a depth of about 4 km are supersaturated with respect to calcium carbonate (Broecker et al., 1979). This would facilitate precipitation of calcium carbonate for any additional input of CO₂ through the atmosphere/ocean interface, and thereby oceans will consume any excess CO₂ in the atmosphere. In the global carbon cycle models this is not accounted for (e.g. Oeschger and Siegenthaler, 1975).

CO₂ in the atmosphere is in chemical equilibrium with carbonic acid dissolved in the hydrosphere (sea, lakes, rivers, etc.) (e.g. Ohmoto and Rye, 1979; Gonfiantini, 1981; Mozeto et al., 1984; Etcheto and Merlivat, 1988; Horita, 1989), which again is in chemical equilibrium with calcium carbonate in water, in lime shells of aquatic organisms, and in limestone (see e.g. Rubey, 1951; Garrels and Thompson, 1962; Garrels and Christ, 1965; Pytkowicz, 1967; Stumm and Morgan, 1970; Plummer et al., 1978; Plummer and Busenberg, 1982; Talsman et al., 1990). Several chemical reactions stabilizing this atmosphere/ hydrosphere equilibrium have been working at least during the last 600 million years (Holland, 1984).

The inorganic dissolved carbon in the ocean (aq) is exchanged between atmospheric CO₂ (g) and solid calcium carbonate (s) by the following chemical reactions:

Partial reactions:



Net reaction:



In the current global carbon cycle models the last partial chemical reaction is neglected. Any additional CO₂ entering the ocean from the atmosphere will have the potential of precipitating calcium carbonate according to the Principle of le Châtelier (average ocean depth 3.8 km; average calcite saturation depth 4 km). This is why the vast sedimentary CO₂ reservoir has been accumulated on the Earth's surface throughout its history. The ultimate source is CO₂ constantly degassed from the Earth's interior. The atmosphere represents just a small short-term CO₂ reservoir in this process. Without oceans and sediments the partial pressure of atmospheric CO₂ on Earth would be several tens of atmospheres, like on Venus.

The CO₂ of the Earth's interior is stored in the form of solid carbonates. A considerable amount of CO₂ is expected to be stored in the mantle in the form of magnesite MgCO₃ (Katsura and Ito, 1990). Mantle CO₂ moves in the form of carbonated magma. Such a melt may dissolve up to 8 weight % CO₂ (Eggler and Mysen, 1976) at 45 kbar (1 bar = 10⁵ Pa), at about 125 km depth. The CO₂ transported upward would be released from the carbonated magma as volcanic gases and fluid inclusions when the magma reaches a depth of less than 70 to 90 km, where the carbonates become unstable (Wyllie and Huang, 1976). When

the magma erupts at the surface it can only hold 0.01 to 0.001 weight % CO_2 dissolved (Harris and Anderson, 1983), implying that up to 99.99% of the CO_2 in mantle-derived magmas will be degassed to the atmosphere. In this way CO_2 has been successively extracted from the mantle by volcanism throughout the Earth's history, and is still being degassed today.

Only in the upper 75 m layer of the ocean there is enough calcium to bind more than 3000 GT C. This is a large potential sink for the annual anthropogenic 6 GT C. One should note that this reservoir is continuously replenished from other parts of the ocean and from the lithosphere. Adding CO_2 to the water will increase its buffer capacity and enhance its ability to moderate the atmospheric CO_2 level (Butler, 1982). The maximum buffer capacity is achieved at 2.5 to 6 times the present partial pressure of atmospheric CO_2 , depending on temperature and alkalinity. According to Maier-Reimer and Hasselmann (1987) the borate system increases the ocean storage capacity for CO_2 by more than 20% (compared with a borate-free ocean).

The vast calcium carbonate buffer is not the only buffer acting in the atmosphere/hydrosphere/lithosphere system. The Earth has a set of inorganic geochemical equilibrium systems working simultaneously. The equilibrium system anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ – kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ at the pH of sea water has a buffer capacity one thousand times higher than that of a 0.001 M carbonate solution (Stumm and Morgan, 1970). In addition, there are clay mineral buffers, and the calciumsilicate + $\text{CO}_2 \rightleftharpoons$ calciumcarbonate + silica buffer (e.g. MacIntyre, 1970; Krauskopf, 1979). These serve as "security nets" under the main buffer controller: the CO_2 (gas) – HCO_3^- (aqueous) – CaCO_3 (solid) buffer system (Segalstad and Jaworowski, 1991). This suite of mineral buffers attain, in principle, an infinite buffer capacity (Stumm and Morgan, 1970). As Kramer (1965) expresses it: "A few simple calculations will show that only very large additions or subtractions of carbon dioxide (from the lithosphere) could overwhelm these equilibria".

Current global carbon cycle models are made to fit the assumption that the level of CO_2 in the pre-industrial atmosphere was about 280 ppmv, and that due to a "buffer factor" the ocean can remove only about 10% of the atmospheric CO_2 added by man's activities (e.g. Siegenthaler and Oeschger, 1987). This "buffer factor" was calculated by assuming that the chemical interaction of atmospheric CO_2 is limited only to the reactions $\text{CO}_2 \rightleftharpoons \text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-}$ in the 75 m thick upper ocean layer, and by neglecting other seawater species and buffer systems, and by assuming that CO_2 removal will be limited to this upper layer.

In the carbon cycle models it is assumed that the ventilation of the deep ocean water is very slow and that the deep circulation is effective on time scales of 100 – 1000 years (IPCC, 1990). However, recent measurements of ^{14}C and ^{39}Ar (with the half-lives of 5730 and less than 270 years, respectively) in the oceanic water demonstrated that the turnover time of the Atlantic deep-water below 4250 m is about 30 years, and that the inflow rate of the north east Atlantic deep water is about 10^{14} m^3 per year (Schlitzer et al., 1985). Only this inflow transfers about 10 GT total CO_2 per year.

The assumption on the low pre-industrial CO_2 and on the "buffer factor" produce modeling results which are incompatible with atmospheric measurements and actual anthropogenic emissions of CO_2 . The

modeling results indicate that about 50% of the man-made CO_2 remained in the atmosphere since the middle of 18th century, and that only 10% was removed by the ocean. Thus the carbon cycle models are unable to account for the "lacking" 40% of man-made CO_2 . According to Broecker et al. (1979) 25 to 100 % of fossil fuel CO_2 released in the atmosphere is not accounted for by the current carbon cycle models. This demonstrates a serious weakness of the models and indicates that the assumptions on which the models are based (i.e. low pre-industrial atmospheric level, and low capability of the ocean to remove man-made CO_2 from the atmosphere) may be wrong.

The solubility of CO_2 in water can be expressed by Henry's Law Constant, K_H (Drummond, 1981; Henley et al., 1984; Barta and Bradley, 1985). This constant numerically expresses the decreasing solubility of CO_2 in water for increasing temperature (up to about 200 °C) and the equilibrium partitioning of CO_2 between atmosphere and water (1:32 at 25°C; Krauskopf, 1979). As temperature rises, less CO_2 may remain in the water. Therefore a warmer ocean will degas CO_2 to the atmosphere. This "thermally driven solubility pump" accounts for approximately 70% of the total ocean degassing, while the remaining 30% is accounted for by the organic nutrient "biologic pump", according to Volk and Liu (1988). The thermal solubility pump and the biological pump increase the atmospheric level of CO_2 when the sea and air temperatures rise due to a natural climatic fluctuation. The powerful negative feedback mechanisms, e.g. due to an increase in cloudiness, lower the temperature and keep the naturally fluctuating global air temperature in balance (see Chapter 1).

It has been estimated that approximately 4000 GT of CO_2 was fluxed from the ocean *via* the atmosphere to the continental biosphere during transition from a glacial to an interglacial stage (Faure, 1990). Other natural carbon fluxes (weathering, volcanism, carbonate sedimentation and dissolution, degassing by metamorphism, etc.) are not included in this figure. The current natural CO_2 flux between the atmosphere and ocean is about 100 GT C per year, and between the atmosphere and the terrestrial biosphere about 63 GT C per year. Anthropogenic releases of CO_2 of about 6 GT C are small in comparison to these natural fluxes.

The biological activity in the ocean, together with gravitational forces, act as a pump for keeping CO_2 out of the atmosphere (e.g. Sakshaug, 1990). Gorshkov (1982) estimated that due to fixation of man-made carbon by oceanic phytoplankton the maximum atmospheric CO_2 concentration could never exceed about 390 ppmv. If these biologic activities were removed, the partial pressure of CO_2 would be increased by a factor of 5 (Eriksson, 1963). Hence, variations in marine biologic activity alone could account for larger variations in the amount of atmospheric CO_2 than anthropogenic contributions from burning fossil carbon fuels at the current rate.

The equilibrium partition coefficient for the CO_2 distribution between atmosphere and ocean is approximately 1:50 (Revelle and Suess, 1957; Skirrow, 1975). This partition coefficient can be used to set an upper limit for how much the CO_2 concentration will rise in the atmosphere if all available fossil carbon fuel (coal, petroleum, gas) were burned. In order to permanently double the current level of CO_2 in the atmosphere under chemical equilibrium conditions, the atmosphere must be supplied with approximately

51 times the present amount of CO₂ if equilibrium should be attained. In order to keep the partition coefficient (air:sea = 1:50) constant at the double amount of CO₂ in the air, the new ratio would have to be 2:100. In other words an increase of one unit in air leads to an increase of 50 units in the sea; a total of 51 units has to be supplied.

As can be seen in Table 1, all available fossil fuel carbon amounts to 11 times the amount of carbon in the atmospheric CO₂. Therefore, mankind does not have enough fossil fuel to double the current level of atmospheric CO₂ under equilibrium conditions, all other factors held constant. If the total fossil fuel reservoir of 7200 GT C were burned during the next 300 years, only the dissolved organics (carbon pool of about 1000 GT C) would consume all man-made CO₂, due to the fact that this period covers 6 to 15 turnovers of the upper-ocean pool of dissolved organic carbon, based on radiocarbon (¹⁴C) studies (Toggweiler, 1990; Druffel and Williams, 1990; Rau, 1991). However, the vast oceanic dissolved inorganic carbon reservoir of 38,000 GT C indicates that the sea is a much more powerful sink for the atmospheric CO₂. Hence, it is unlikely that permanent doubling of the amount of atmospheric CO₂ is attainable by human activities. Similar doubts have been expressed by Abelson (1990), and earlier by Gorshkov (1982) (see also Kondratyev 1988).

The transfer of CO₂ from the atmosphere to the hydrosphere is facilitated by leaching with cloud droplets. The average diameter of a cloud droplet is 20 µm (Battam, 1979), and its mass is 4.2 x 10⁻⁹ g. The mass of ~5 x 10²⁰ g of global annual precipitation corresponds to about 10²⁹ droplets. The total surface of these droplets is about 10¹⁴ km², i.e. ~275,000 times greater than the surface of the ocean. The high solubility of CO₂ in water at low temperature and enormous surface of droplets exposed to atmospheric CO₂ must contribute to a flow of inorganic carbon from the atmosphere to the hydrosphere. The total amount of CO₂, which might be dissolved in the global annual precipitation, may reach ~0.3 GT CO₂.

Another sink for CO₂ is weathering of silicate minerals. It has been demonstrated by Walker et al. (1981) that the partial pressure of CO₂ in the atmosphere is buffered, over geologic time scales, by a negative feedback mechanism in which the rate of weathering of silicate minerals (followed by deposition of carbonate minerals) depends on surface temperature. The higher the temperature the greater the removal of CO₂ from the atmosphere by deposition of carbonates. This negative feedback is an important factor in the long-term stabilization of the global surface temperature. Schwartzman and Volk (1989) have suggested that biota amplify this negative feedback.

Holland (1984) has tested whether the atmospheric CO₂ content has been extremely low or extremely high during the Earth's history. At low partial pressure of CO₂ gypsum CaSO₄•2H₂O would be formed at the expense of calcium carbonate. This has not been found in marine sediments. At high partial pressure of CO₂ dolomite CaMg(CO₃)₂ would be expected to precipitate directly from the ocean instead of calcium carbonate (aragonite or calcite). This has not been found either. The conclusion is that the atmosphere/hydrosphere equilibria operating at the Earth's surface today, have been working through hundreds of millions of years, even during periods of intense volcanic release of CO₂. A correlation between increased volcanic production and increasing marine carbonate sedimentation has been found by Budyko et al. (1987).

3. AIR CONCENTRATIONS OF CO₂

3.1 CONTEMPORARY MEASUREMENTS

An important component of the "greenhouse" warming hypothesis is the analysis of CO₂ concentrations in the atmosphere. The first large scale measurements were started in 1955 in Scandinavia (Bischof, 1960). Since 1958 systematic monitoring of CO₂ has been made at the Mauna Loa Observatory in Hawaii (Bacastow et al., 1985) and later at several other stations (Boden et al., 1990). One should note that nondispersive infrared techniques now used at Mauna Loa and other stations are not direct chemical measurements. The results may be influenced by the presence of other "greenhouse" gases in air samples with absorption bands overlapping those of CO₂. This is suggested by results from 19 Scandinavian stations (Bischof, 1960) in which a sudden increase in CO₂ concentration was observed after a chemical method was replaced by the infrared (IR) technique in 1959. Other IR-absorbing gases than CO₂ have continuously increased their abundances in the global atmosphere. This could have given continuously increasing and too high "CO₂ readings" at Mauna Loa and other stations using the infrared technique. Independent non-instrumental chemical analyses of the reference gases and flask samples of the atmosphere have not been seen reported, and should certainly be required.

The annual mean concentrations reported from the Mauna Loa observatory increased from 315.55 ppm in March 1958 to 351.45 in January 1989 (Pales and Keeling, 1965; Keeling et al., 1989; Thoning et al., 1989; Boden et al., 1990). The Mauna Loa data have been regarded as representative for the global concentration of CO₂ in the atmosphere. This seems to be rather doubtful, due to the fact that the site is exposed to vast local natural emissions of CO₂, and also CO₂ from man-made sources.

The published results of the Mauna Loa measurements indicate that the atmospheric CO₂ load has systematically increased about 10% during the past 30 years. Together with concentrations of CO₂ found in air bubbles trapped in glacier ice, these results have often been used as a proof that the atmospheric CO₂ level has increased by 25% since about 1850 (e.g. Schneider, 1989; IPCC, 1990). The predictions that the atmospheric CO₂ level will double around the year 2030 are based on extrapolating the combined results of glacier and air measurements, and on the assumption that the 25% increase is solely due to man-made sources. Combining the glacier data with atmospheric measurements into one smooth curve was made possible only by assuming that the air entrapped in the ice is 95 years younger than the age of ice in which the air was entrapped. However, this assumption was found to be incorrect (Jaworowski et al., 1992; see also discussion in 5.2). Without this assumption the CO₂ concentration in air recovered from the 19th century ice is the same as that at about 1980 in the Mauna Loa record.

The measurements in Scandinavia were carried out by a chemical method, different from that used at Mauna Loa. Therefore, it is especially interesting to compare them. For 19 stations in Scandinavia the total annual mean CO₂ concentrations were 326 ppmv in 1955, 321 ppmv in 1956, 323 ppmv in 1957, 315 ppmv in 1958, and 331 ppmv in 1959 (Bischof, 1960). The first Mauna Loa annual mean for 1959 was 315.83 ppmv,

316.75 ppmv for 1960, 317.49 for 1961, 318.30 for 1962, and 318.83 for 1963. There was an apparently decreasing trend in Scandinavia during the first four years before introducing the infrared technique, with a marked rise after its introduction, and a steadily increasing trend at Mauna Loa where only the infrared technique was used. No increasing trend in the CO₂ air concentrations between 1957 and 1961, measured by the infrared technique, was observed in Scandinavia at altitudes of 1000 to 3000 meters (Bischof, 1962). The decreasing trend in Scandinavia could hardly be due to errors in the analysis, which had an accuracy not much different from that of the technique used at that time at Mauna Loa. The cause of the inconsistency of the Scandinavian and Mauna Loa data remains unclear.

As the Mauna Loa data are extensively used as representative for the average global air concentration of CO₂, we discuss here the accuracy of the Mauna Loa measurements, to illustrate the difficulties involved in estimating levels of CO₂ in the atmosphere.

The observatory is located at the slope of the active Mauna Loa volcano, which has had on the average one eruption every three and half years since 1832 (Encyclopaedia Britannica, 1974; Simkin et al., 1981). Following an eruption in 1975, the Mauna Loa volcano remained at rest until March 1984, when about 220 million tons of lava covered an area of about 48 km². Pre-eruption activity had been occurring since about 1980 (Koyanagi and Wright, 1987; Koyanagi et al., 1987). The CO₂ content of volcanic gases emitted, associated with various types of lava, was reported by Rubey (1951). The concentration of CO₂ in the gases emitted from the Mauna Loa and Kilauea volcanos of Hawaii reaches about 47%. This is more than 50 times higher than in volcanic gases emitted in many other volcanic regions of the world. The reason for this is the alkaline nature of this volcanism, strongly associated with mantle CO₂ degassing. The Kilauea volcano alone is releasing about 1 MT CO₂ per year, plus 60 – 130 kT SO₂ per year (Harris and Anderson, 1983).

The observatory is also exposed to permanent CO₂ vents from the volcanic caldera and a rift zone situated only 4 km upslope from the observatory (Pales and Keeling, 1965), and from some distant sources downslope (Keeling et al., 1976). Pales and Keeling (1965), in their description of methodology and the sampling site, did not mention that the world's largest active volcanic mass, Kilauea, with the largest and most active volcanic crater on Earth (5 km long and 2 km wide) is situated only 27 km southeast from the Mauna Loa observatory. Frequent eruptions of this volcano occurred during the 1960s and 1970s. CO₂ emission from Kilauea also occurs in non-eruption periods (Decker and Koyanagi, 1983; Decker et al., 1987). Emissions of up to 5000 tons of CO₂ per day were recorded from the summit crater of this volcano in non-eruption periods (Gerlach and Taylor, 1990).

More recently, increased activity of Kilauea begun in January 1983 and continued throughout 1984. There were 16 major gas-charged eruptions in 1984, with fountains of lava several hundred meters high, and with an average production of lava of about 10 million tons per episode. A word "vog" (from "volcanic fog") has been coined on the island of Hawaii to define the volcanic haze that has been hanging over the island since Kilauea's latest eruptive phase began in 1983. This "vog" consists of water vapor, CO₂, and SO₂. The conditions might resemble a mild city smog (Bendure and Friary, 1990). Such conditions should influence

the CO₂ readings at Mauna Loa Observatory. The question arises how the air at Mauna Loa can give a representative average global atmospheric CO₂ level.

To account for the influence of volcanic emissions from the neighboring 10 km long rift zone and caldera at Mauna Loa, Pales and Keeling (1965) calculated an increase in CO₂ concentration of 2 ppm for a certain "weather type", which is about three times higher than the observed 0.68 ppm average increase per year. The eruption events of the Mauna Loa and Kilauea volcanoes, or for quiescent emission of CO₂ from the gigantic Kilauea crater, were not discussed by these authors. Eleven years later Keeling et al. (1976) mentioned the prolonged period of Kilauea activity which commenced in November 1967 and ended in March 1971. In March 1971 a locked chain gate was erected across the road to the Mauna Loa observatory 0.5 km from the CO₂ intakes, to control the automotive traffic. A current tourist guide instructs tourists: "Park in the lot below the weather station [because] the equipment used to measure atmospheric conditions is highly sensitive to exhaust" (Bendure and Friary, 1990). (The chain was not in use and cars were parked immediately under the CO₂ intakes when one of the present authors visited the site in March 1992).

An example of the variations of hourly average atmospheric concentration of CO₂ during three consecutive days at Mauna Loa is shown in Figure 1. It demonstrates that it seems extremely difficult at this locality to determine values representing global concentrations. This point is further illustrated by Figure 2, where the effect of data selection at the Cape Matatula Station in Samoa (another volcanic island, with Hawaii-type hot-spot volcanism) is presented. The description of the methods used at both stations for elimination of irregularities to get a representative value confirms this conclusion.

The effects of different kinds of local vegetation on the concentrations of CO₂ in air have not been satisfactorily treated, and a number of features of the published curves for atmospheric variation of CO₂ through approximately the last 30 years have not been explained (Keeling et al., 1989). Pales and Keeling (1965) discuss the depletion of atmospheric CO₂ by a tropical forest downhill from Mauna Loa Observatory, which was supposed to cause "dips" in their readings. Grassland production of CO₂ may have a large influence on CO₂ levels in the air, as well as respiration and decay of organic matter. Daily fluctuations of CO₂ concentration over a grassland were found to reach 40 ppm, and the seasonal variations (between June and September) reached about 25 ppm (Spittlehouse and Ripley, 1977). Daily variations over a wheat field can almost double the amount of CO₂ in the air (Fergusson, 1985). Pales and Keeling (1965) noticed the existence of CO₂ sources at the Mauna Loa observatory itself, such as exhausts of a diesel engine-driven generator and automobile pollution which have become a problem (Keeling et al., 1976). In view of these points of criticism, the claim of Pales and Keeling (1965) that "the observatory is thus an excellent, if not ideal, site for measuring CO₂ in the upper air" seems to be overly exaggerated.

Throughout the whole period of measurements the results were "edited" (an expression used by Bacastow et al., 1985) to account for local disturbances causing both higher and lower CO₂ concentrations. As Pales and Keeling (1965) stated, the measurements are clearly locally influenced. The authors applied "omissions of variable periods from the daily averages" to eliminate both high and low readings. In Figure 1 about 80% of the readings were omitted. In addition, days without data constitute 17% of the record. For

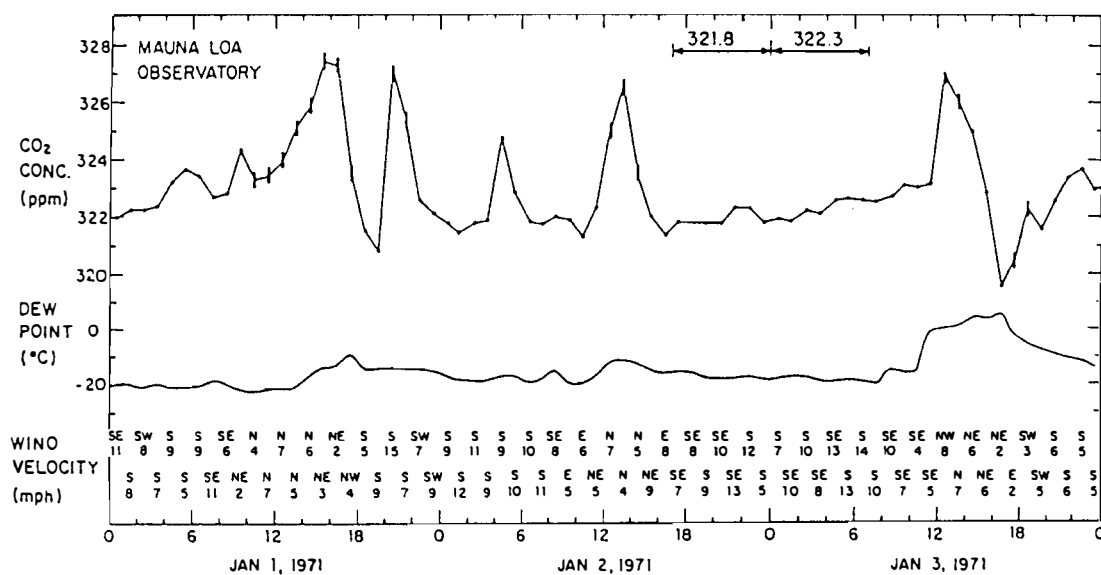


Figure 1. Hourly average atmospheric CO₂ concentration at Mauna Loa (Hawaii). Vertical bars indicate periods rejected from the records, as local CO₂ releases were suspected. Horizontal arrows indicate "steady periods" supposed to give a more representative concentration. (After Keeling et al., 1976.)

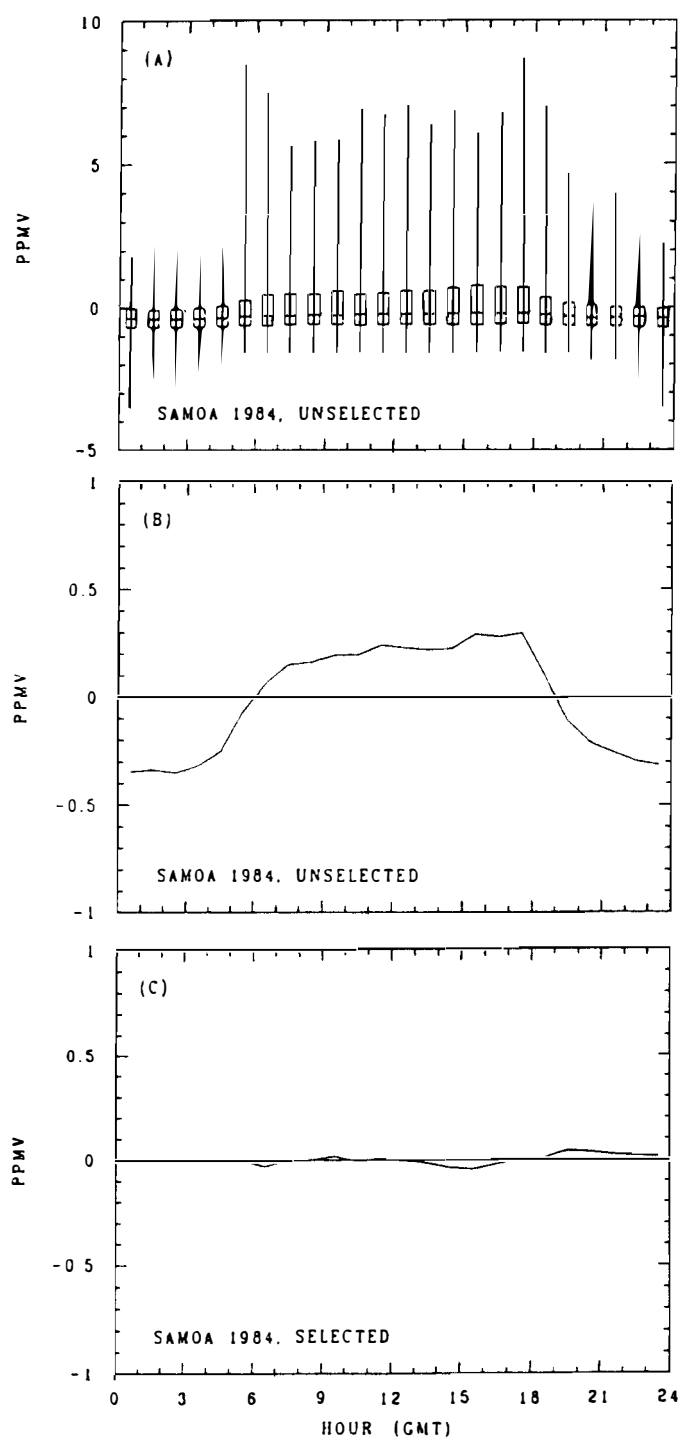


Figure 2. Results of the CO₂ data selection procedure for 1984 at Cape Matatula, Samoa. A: unselected hourly averages. The vertical lines represent the full range, while the boxes represent the range of the middle half of the data. Indicated are the 25th percentile, median, and 75th percentile points. B: average daily cycle for the entire year of unselected data. C: average daily cycle for the entire year after selection. (After Waterman et al., 1989).

these lacking days the values were assigned by linear interpolation (Keeling et al., 1976).

The values that were omitted were defined as "measurements that occur when the air trace shows significantly more variation than the reference gas" (Bacastow et al., 1985). When estimating daily averages the "too high" or "too low" values were eliminated by "visual inspection". This clearly introduced a subjective factor in the estimates of temporal trends.

Other long term measurements of atmospheric CO₂ were recorded at stations not exposed to vast local volcanic emissions of CO₂. These measurements show an increasing long-term trend similar to that of the Mauna Loa data, but with different amplitudes for the seasonal changes. However, an "editing" process similar to that used for the Mauna Loa record was applied also to the data from these other stations to account for (assumed) local disturbances.

It is difficult to understand that the effect of a powerful natural injection of 6 GT of CO₂ (equivalent to 2 GT C) by the El Niño – Southern Oscillation (ENSO) 1982–1983 event (Gaudry et al., 1987), and of nine other ENSO events, are not directly visible in the Mauna Loa and the South Pole records (Siegenthaler, 1990). On the other hand, it has been claimed that the records detect the annual anthropogenic CO₂ releases, which are just 2–3 times higher than the ENSO events. This may mean that the "editing" procedure produces records not reflecting important large-scale CO₂ variations in the atmosphere. The anthropogenic emissions are small compared to natural CO₂ fluxes, and it cannot be excluded that the reported increase in atmospheric CO₂ is due to fluctuation of the natural fluxes. The tacit assumption in the "greenhouse" warming hypothesis that the natural CO₂ fluxes are constant, is unrealistic.

In order to test the Mauna Loa CO₂ data we compared them with fossil fuel CO₂ emission data compiled by Boden et al. (1990) (Figure 3). For this comparison we assume that the Mauna Loa data represent the average global atmospheric CO₂ concentration. The annual CO₂ emissions into the atmosphere from fossil fuel burning and cement production increased almost continuously from about 2.6 GT C per year in 1960 to 5.9 GT C per year in 1988. The rate of increase at Mauna Loa was less between 1973 and 1975, and turned into a decrease between 1979 and 1983. The annual increases of the atmospheric CO₂ mass inferred from the Mauna Loa data (referred to as "Mauna Loa" atmospheric CO₂ mass) revealed a totally different character (Figure 3 A). These increases fluctuated irregularly between 1.0 GT C in 1963 to 5.5 GT C in 1988, with highs and lows not related to industrial emissions (e.g. in 1963, 1969–72, 1973–74, 1981–83, and 1986).

During the so called "petroleum crisis" in 1973 – 1975 the annual increase of the CO₂ atmospheric mass, inferred from Mauna Loa data ("Mauna Loa" atmospheric CO₂ mass), decreased from about 4.5 to about 1 GT C whereas the real fossil fuel CO₂ emissions were nearly constant at that time (Figure 3 A). The sudden deep drop between 1973 and 1974 in year to year changes of annual increases of "Mauna Loa" atmospheric CO₂ mass, when the changes in real CO₂ emissions from anthropogenic sources were stable (Figure 3 B), may be an effect of the subjective factor in the "editing" of the Mauna Loa data.

That the Mauna Loa data are not representative for the man-made emissions is strongly suggested by the character of the interannual changes in the Mauna Loa data, which are highly different from the way the fossil fuel CO₂ emissions vary from year to year. The equilibration between CO₂ concentration in the

atmosphere and the dissolved inorganic carbon in the sea is very short (about three quarters of a year according to Bolin, 1982). Therefore one might expect that most of the annual man-made perturbation in atmospheric CO₂ would be visible in the Mauna Loa data in the same, or in the next year, provided the man-made CO₂ fluxes are not masked by the natural fluxes. Figure 3 B shows sharp upward and downward interannual changes in the "Mauna Loa" atmospheric CO₂ mass. The amplitude of these changes reaches up to about 5.5 GT C per year. These dramatic "Mauna Loa" CO₂ changes are not reflected in the more steady annual emissions of fossil fuel CO₂, which has a maximum amplitude of 0.28 GT C. In about half of the years the "Mauna Loa" CO₂ mass changed in a direction opposite to that of fossil fuel CO₂ emissions.

These discrepancies suggest that the Mauna Loa record was strongly influenced by something else than fossil fuel CO₂. As indicated before, one possibility is the natural flux of CO₂ (e.g. CO₂ outgassing from the ocean and the interior of the Earth).

3.2 NINETEENTH CENTURY CONCENTRATIONS

In the 19th century the measured CO₂ concentrations in the atmosphere ranged from ~250 to 550 ppmv (Fonselius et al., 1956). On the basis of these measurements (mainly carried out at Montsouris observatory near Paris) the pre-industrial level of CO₂ was estimated by Callendar (1940, 1958) to be 292 ppm. According to Callendar (1958) the 19th century data do not "show a significant trend between 1870 and 1900", i.e. in a period when the annual emissions of CO₂ from fossil fuels increased by a factor of 3, from 0.15 to 0.5 GT of carbon (Elliott, 1983).

Callendar's estimate of 292 ppm for pre-industrial CO₂ atmospheric level was obtained by applying a selection method. This method was questioned by Slocum (1955), who indicated that without such selection these data averaged 335 ppm. Slocum (1955) pointed out that from a set of 26 19th century averages Callendar rejected 16 that were higher than the global average of 292 ppm, and only 2 that were lower. On the other hand, from the 20th century set Callendar rejected 3 averages that were lower than his global average of 317 ppm, and none that was higher. This bias in the selection method is demonstrated in the set of 19th century data compiled by Fonselius et al. (1956) (Figure 4).

The Montsouris data show large shifts of monthly means (>10 ppm from one month to the next) and they show no seasonal variations. This is incompatible with modern records showing much less daily scatter and a clear seasonality (Waterman, 1983). The most obvious jump occurred at Montsouris between June and July 1890, when a change of 27 ppm was reported. This change is about the same as the increase observed at the Mauna Loa observatory during 22 years from 1958 to 1980. Some of the Montsouris measurements indicate extremely high or low values (355 ppm and 243 ppm, respectively). This has been interpreted as evidence of analytical and sampling shortcomings (Stanhill, 1983).

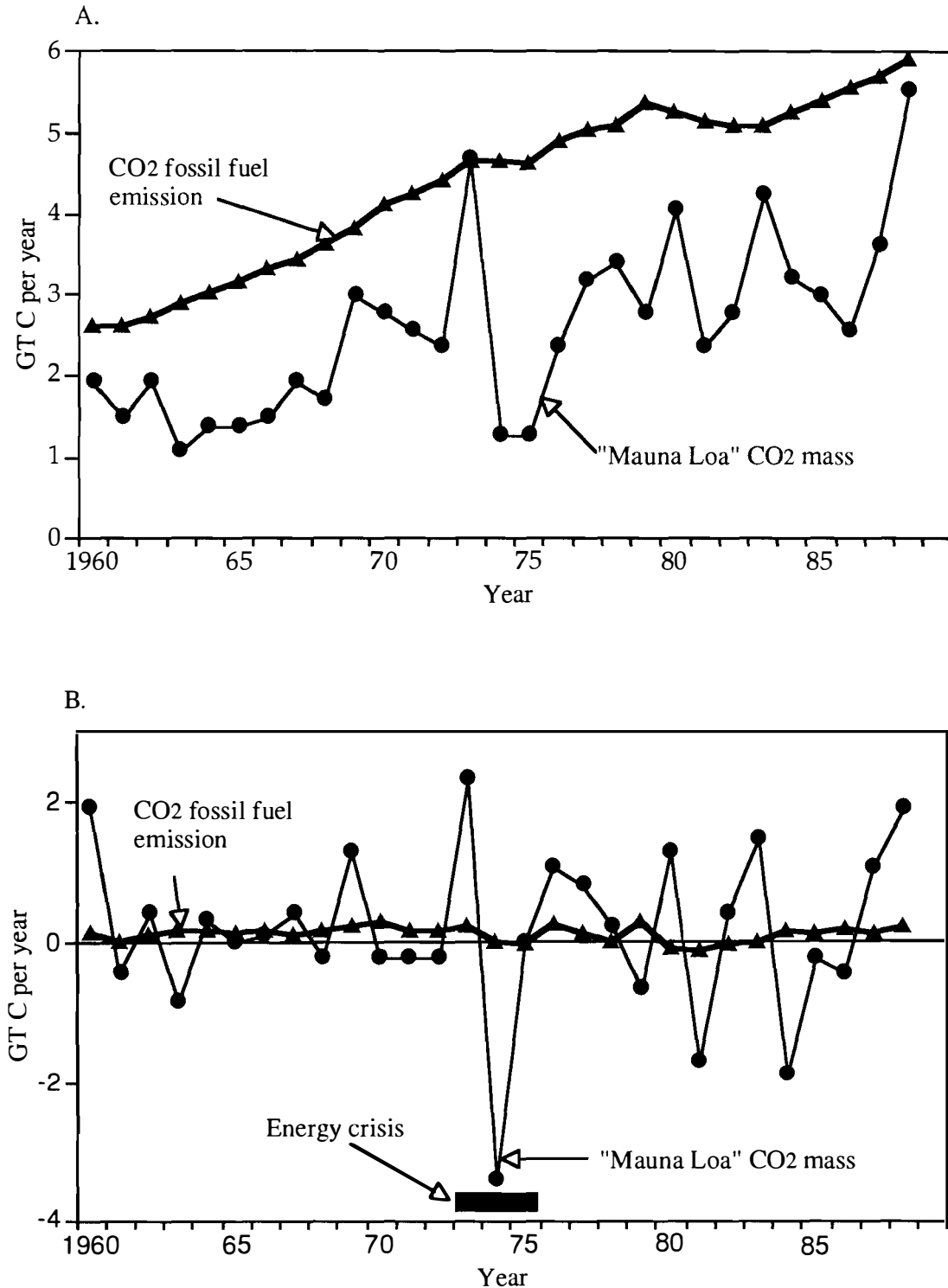


Figure 3. Mauna Loa representation of global atmospheric CO₂ mass, and fossil fuel CO₂ emissions. A: Annual increase in "Mauna Loa" atmospheric CO₂ mass and annual emissions of fossil fuel CO₂. B: Year to year changes in "Mauna Loa" atmospheric CO₂ mass increase and fossil fuel CO₂ emissions; the ordinate represents the difference between one year and the previous year. The "Mauna Loa" atmospheric CO₂ mass was calculated assuming that 1 ppmv CO₂ corresponds to an atmospheric mass of 2.12 GT C. Calculated from data in Boden et al. (1990).

In 1880 and 1881 Müntz and Aubin determined CO₂ in the center of Paris. The measured concentrations averaged 62 ppm more than those at the same period at Montsouris. Of their ten non-urban sites, seven reported CO₂ concentrations greater than at Montsouris, the mean difference being 12 ppm. In Paris the concentrations recorded in 1880 and 1881 averaged 325 ppm (Wigley, 1983).

It is difficult to believe that a monthly mean of 355 ppm for December 1878 and a mean of 243 for April 1880, reported for the Montsouris Observatory, are truly representative of global background values (Waterman, 1983). The Montsouris investigators were probably not running any blanks or duplicate measurements that could shed light on the precision of their measurements.

The chemical method used at Montsouris was similar to the procedure used by Müntz and Aubin. This method could lead to erroneously low results due to incomplete stripping of the CO₂ from the airstream by a reaction with KOH. Another source of error was probably a reaction of the reagents on the laboratory apparatus (Waterman, 1983). The enormous temporal scatter of the Montsouris results (of 27 ppm) and the geographical scatter of the Müntz and Aubin data (of 40 ppm) do not represent the "natural noise", but was due to sampling and analytical shortcomings, and indicates that these data are less reliable than 20th century measurements.

It is interesting to note that there is a tendency to choose a low average value for the CO₂ concentration in 19th century atmosphere because "the most compelling support for a 270 ppm pre-industrial CO₂ level comes from direct measurements of CO₂ in the ice cores" (Wigley, 1983). But those who measured CO₂ in the ice cores also preferred to select as true the lower values, because they were "within the range of the estimated [by Callendar, 1958] pre-industrial atmospheric content of 290 ppm" (Berner et al., 1978).

This demonstrates that a subjective factor biased the CO₂ values chosen by the 20th century researchers, and resulted in a too low estimate of its pre-industrial level.

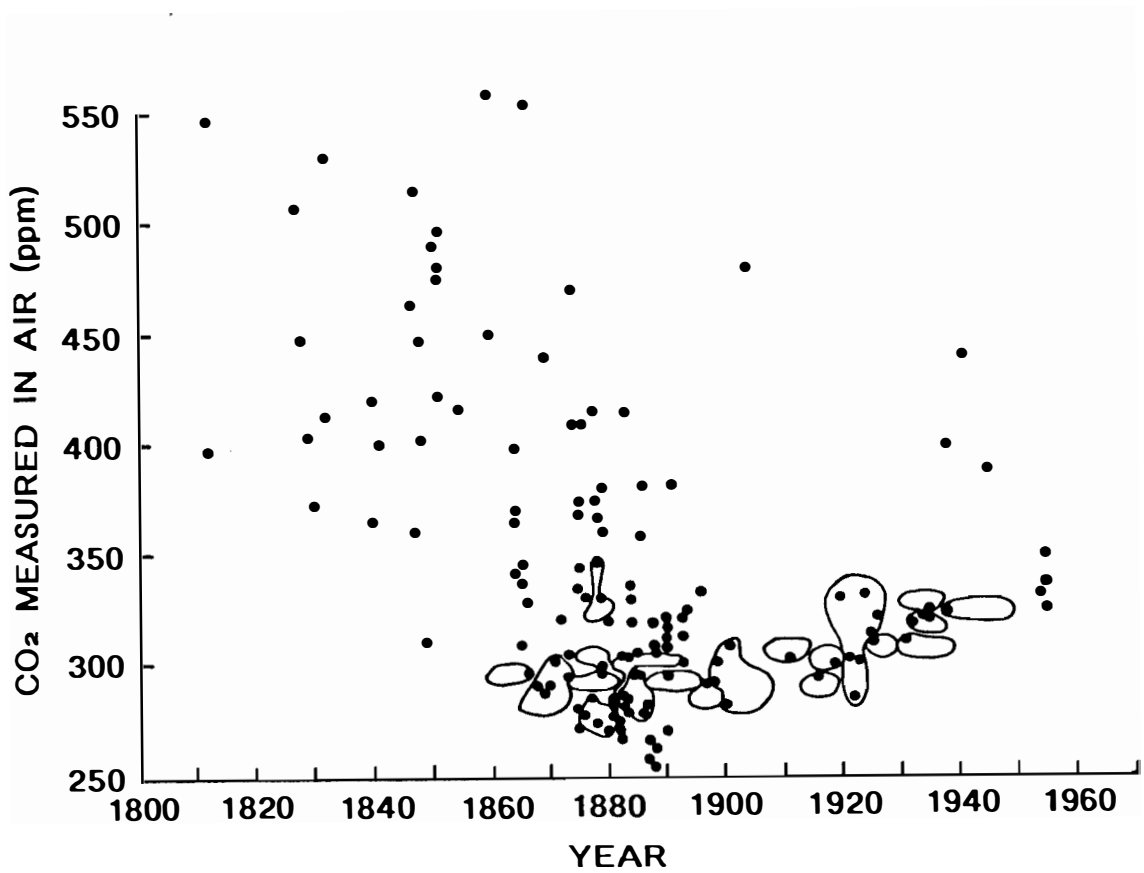


Figure 4. Average atmospheric CO₂ concentrations measured in the 19th and 20th century. Encircled are the values used by Callendar (1958). Redrawn after Fonselius et al. (1956).

4. TREE RINGS AS INDICATORS OF CO₂ IN THE ATMOSPHERE

The stable carbon isotope ratio, $^{13}\text{C}/^{12}\text{C}$, in tree rings was used to calculate the CO₂ contents of the atmosphere in the past. The results of Stuiver et al. (1984) are often used (even in official documents) to draw a curve showing the CO₂ content in the atmosphere during historic time (e.g. Miljøverndepartementet, 1988–1989). The original paper by Stuiver et al. (1984) and other works (e.g. Deines, 1980) demonstrate that contemporaneous trees from the same period show large variations in their carbon isotope ratios. Stuiver et al. (1984) emphasize that after normalizing and averaging the data from different trees, there was still a remaining variability in the data resulting in a standard error of ± 16 ppm (assumed 68 % confidence level) in the calculated CO₂ contents (analytical and sampling errors not included). For the computational uncertainty alone, a 95 % confidence level would give ± 31 ppm. A large part of the variation calculated by Stuiver et al. (1984) is less than this statistical uncertainty.

Recent systematic studies on stable isotope geochemistry in plants cast serious doubts on the usefulness of this method in paleoclimatology because of isotopic inhomogeneity in the plants themselves (e.g. Yakir et al., 1989) and post-photosynthetic modifications in the wood cellulose (e.g. DeNiro and Cooper, 1989). A systematic study by Tans and Mook (1980) of carbon isotopic ratios of the complete circle of a single tree ring revealed that the carbon isotope variations were up to 3.5 permil.

The maximum variation in $\delta^{13}\text{C}$ given by Stuiver et al. (1984) for the last 1800 years was 3 permil, most of the variation was within 2 ± 1 permil. The calculated curve for the atmospheric CO₂ variation for the last 1800 years from carbon isotope ratios in tree rings is hence based on isotope variations which are less than the variations expected in a single tree ring. This fact supports objections to the use of tree ring isotope analysis in paleoclimatology.

The $\delta^{13}\text{C}$ methodology calculates the CO₂ contents of the atmosphere through time by isotopic mass balance calculations in a simplified physical box model (e.g., Oeschger et al., 1975) between the atmosphere, biosphere and the sea at constant temperature. The ratios of light stable isotopes, like the carbon isotopes, are strongly changed by temperature. This is the reason why such isotopes find their major use in science as paleothermometers. The surface temperature of the Earth has varied considerably throughout the last 1800 years (see Figure 9). A temperature change of a few degrees C can account for the observed carbon isotope variations by Stuiver et al. (1984). Variations in rainfall would have influenced photosynthesis and hence the resulting carbon isotope ratios of the tree cellulose (governed to a large extent by biologic kinetic isotope effects). The model also neglects CO₂ releases (or accumulations) from the lithosphere and the Earth's interior, the largest reservoirs of carbon involved. Furthermore, the model assumes that the global source of CO₂ always has a constant carbon isotopic composition. With so many sources and sinks of carbon, each with its distinct carbon isotopic signature (Ohmoto and Rye, 1979), this assumption may be an oversimplification.

Finally, the carbon isotopic composition of corals and contemporaneous trees do not correlate (Nozaki et al., 1978). However, they should correlate if all the assumptions were valid and the methods suitable. It

must be concluded that the CO₂ contents in the atmosphere calculated from carbon isotope analysis of tree rings cannot be considered a valid tool in paleoclimatology, and cannot be used as evidence of changing atmospheric CO₂ levels.

5. CO₂ IN GLACIER ICE

Studies of CO₂ concentrations in glacier snow and ice are a cornerstone of the increasing "greenhouse effect" hypothesis. Results from these studies are the most important input parameters in the models of the global carbon cycle, and are used as the basis for estimates of climatic change caused by human activities (e.g. IPCC, 1990). Therefore, they deserve a wider discussion.

The early determinations of CO₂ in air bubbles trapped in glacier ice, carried out in the 1950s to the 1970s, recorded much higher concentrations in the pre-industrial samples than the mean value of about 290 ppm estimated by Callendar (1958) for the nineteenth century air. It was during the 1980s that the CO₂ levels in the pre-industrial ice began to be interpreted as being in agreement with the Callendar estimate.

The first CO₂ studies in glacier ice were initiated at the University of Oslo, and the first measurements were carried out at the Storbreen glacier in Jotunheimen, Norway (Coachman et al., 1956; Coachman et al., 1958 a; Nutt, 1959). These studies indicated that the CO₂ content in air bubbles in the pre-industrial ice ranged between 200 and 2900 ppm, and that in the older parts of the glacier it was reduced by a factor of three due to leaching by liquid water. In samples of old ice from the Greenland ice cap, Coachman et al. (1958 b) found that the oxygen values were close to those of the present-day atmosphere, but values for CO₂ were twice as high as today. They concluded that the atmosphere might have been richer in carbon dioxide at the time this ice was formed. It was recognized in these early studies that the original composition of the air trapped in the ice is changed due to various physical and chemical processes (Scholander et al., 1961).

Coachman et al. (1958 a) stated that the loss of CO₂ from the ice might occur during melting, both at the site of ice formation and at the older part of the glacier. They also noticed that the ice could be contaminated by organic dust, which subsequently became oxidized, enriching the CO₂ of the air in the bubbles. Hemmingsen (1959) observed a great mobility of CO₂ in the glacier ice, which he supposed to be an effect of diffusion in the intercrystalline liquid brine films. Such films and veins of liquid exist in ice even at extremely low Antarctic temperatures (see below).

Alder et al. (1969) found that CO₂ can be adsorbed at the ice surface and remain adsorbed even *in vacuo*, and that this adsorption is not reversible. This effect might decrease the level of this gas in the air bubbles, and also increase its content in the ice by adsorption from the laboratory air. Alder et al. (1969) and Scholander et al. (1961) found evidence that, in the Greenland ice, oxygen is removed by oxidation of organic matter. This may lead to an increase of CO₂ in the ice.

These early studies posed the question whether glacier ice is a reliable matrix for study of the composition of the ancient atmosphere. As will be seen later, after three decades the question is still entirely open.

5.1 CHANGES IN ORIGINAL GAS COMPOSITION

Stauffer et al. (1984) supposed that, among the factors influencing the CO₂ levels in the air bubbles, are the presence of clathrates (gas hydrates), melt layers, and microbubbles. To this list Stauffer and Oeschger (1985) added adsorption of air components on the firm grain surfaces and enclosing the air during snowflake formation, zone refining processes paralleling crystal growth, interaction of CO₂ with the ice itself, fracturing of the ice, chemical reactions between CO₂ and impurities trapped in the ice, and oxygen exchange between CO₂ and water. They found that the increase of the CO₂ concentration parallels the dust content in all the measured ice cores. They also recognized a dependence of CO₂ levels on the acidity of the ice: the samples showing the highest pH values had the lowest CO₂ contents. But perhaps the most important factor, changing the original composition of atmospheric air trapped in the glaciers, is liquid water present in the ice even at extremely low temperatures.

5.1.1 LIQUID IN ICE AT LOW TEMPERATURES

The Antarctic and Greenland ice cores, used for historical studies of CO₂ changes in the atmosphere, are usually regarded as a steady state closed system in which the original concentrations of this gas are preserved indefinitely. The main argument used in support of this assumption is that the existence of a liquid phase in the polar ice can be neglected at or below a mean annual temperature of –24°C (e.g., Berner et al. 1978; Raynaud and Barnola, 1985). This liquid phase would enable diffusion processes to change the original composition of air contained in the ice. However, liquids are present in Antarctic ice at much lower temperatures (see below), so this argument now seems invalid.

Berner et al. (1978) stated that the high content and wide variations of CO₂ observed in ice could be understood if, during the sintering processes of snow to ice, a liquid phase was present. They believed that with mean annual temperatures at a polar ice cap of –24°C, the influence of the liquid phase can be neglected. This is why the later CO₂ studies in the ice were carried out only on the polar ice caps. This opinion is, however, not correct, in view of the evidence that at low Antarctic temperatures both melt layers and intercrystalline liquids occur in the ice (see discussion below).

Scholander et al. (1961) listed several processes that could change the original composition of gas inclusions in ice. One of their most important findings was an observation of enrichment of CO₂, oxygen, and argon (relative to nitrogen) in air bubbles, by freezing them out from the liquids present in the firm or ice containing dissolved atmospheric gases. They also noticed that supercooled fog, carrying dissolved gases, leads to CO₂ enrichment when freezing on the surface of ice sheets. This is what would be expected in view of the changes in gas ratios when air dissolves in water. On a molar basis the solubility of CO₂ in water at a temperature of 0°C is 73.5 times higher than that of nitrogen, the solubility of oxygen is 2.0 times that of nitrogen, and the solubility of argon 2.4 times higher than that of nitrogen. Therefore, at 0°C the

concentration of oxygen in the air dissolved in water is 35%, and not 21% as in the atmosphere (Hodgman et al, 1962; Weast et al., 1989). Gas ratios different from those in atmospheric air should be characteristic of primary gas inclusions (see below) in ice.

The dissolution of air gases in the liquid contained in ice is likely to start with the formation of snow crystals in the atmosphere. The liquid containing sulfuric acid is incorporated into snow crystals as a film on a solid nucleus or added by riming, and it is expected to remain as a liquid on the outside of the grain crystals (Wolff et al., 1988). Therefore, it seems that at least a part of enrichment of CO₂, O₂ and Ar observed in glacier ice occurs during the atmospheric history of the snow crystals.

In later studies of ice cores from both central Greenland and Antarctica (see e.g. Neftel et al., 1982; Raynaud and Barnola, 1985), melt layers were commonly observed. Also Boutron (1986) notes the possibility of disturbing the old ice deposits in Greenland and Antarctica by percolating water during the summer months. During the Antarctic summer, meltwater was found at a depth of about 1 m in the ice sheet at the station Troll, Dronning Maud Land (Antarctica), 250 km inland, where the summer air temperature was below –20°C (Hagen, 1990). Veins of liquid are also present in the capillary network between ice crystals, even at extremely low temperatures in the Antarctic ice-sheet (Maccagnan, 1981; Mulvaney et al., 1988).

Acid–water mixtures in layers at ice grain boundaries have been found to remain liquid down to the eutectic point of –73°C (Wolff et al., 1988). In Antarctic ice high aqueous concentrations of 4.9 M sulfuric acid (H₂SO₄) were found in veins at triple–junctions, where the ice grains meet (Mulvaney et al., 1988). Using isotopic (¹⁴C) dilution method Shchennikova et al. (1957) found that the solubility of CO₂ in concentrated H₂SO₄ increases with decreasing temperature and increasing concentration. At 20°C and above 85 weight % concentration of acid the CO₂ solubility was found to be about 0.9 ml/ml, i.e., about the same as in distilled water. This indicates that CO₂ from air bubbles trapped in the ice can penetrate into the network of intercrystalline acid brine and its concentration in the air inclusions may decrease with time.

When alkaline dust neutralizes acids in the ice, the resulting salt–H₂O mixtures may cause freezing point depressions. The extent of freezing depression is dependent on the type and concentration of salts in the intercrystalline brines. In this way, the brine can keep its liquid state down to –50°C or even lower (Roedder, 1984; Shepherd et al., 1985; Oakes et al., 1990). When freezing salt aqueous solutions, pure ice crystallizes, leaving a more saline solution. In the sea ice the liquid brine was observed down to a temperature of –70°C (Weeks and Ackley, 1982). This effect may influence the behavior of gases in the deep ice strata. The high content of Na at Vostok (Antarctica) at depths of about 500, 850, and 2000 m coincided with the low CO₂ content recovered from the air inclusions. The low content of Na at the depths of about 1420, 1770, and 1850 m coincided with the increasing CO₂ concentrations (Barnola et al., 1987).

The importance of the discovery of a liquid phase in ice at extremely low temperatures is difficult to overestimate. It suggests that in glacier ice there is a quasi infinite network of liquid–filled veins through which dissolved substances can migrate during long periods of time. Thus the polar ice is composed of water in liquid, solid and gaseous states which are interchanging during the long lifetime of the ice sheets;

a large scale displacement of mass is involved in this interchange (Jaworowski et al., 1992). Therefore, the validity of Antarctic and Greenland ice cores as reliable objects for study of chemical and isotopic composition of the atmosphere of the past epochs is therefore highly questionable.

Considerable knowledge of gas and fluid inclusions in solids has been gained from the geological sciences (e.g. Hollister and Crawford, 1981; Roedder, 1984; Shepherd et al., 1985; Bodnar et al., 1985). The fundamental principle underlying all gas/fluid inclusion studies is that gases and fluids inside the inclusions are representative portions of the gases and fluids present in the phase from which the host mineral grew (provided the gas/fluid is homogenous at the time of trapping). Such inclusions are called primary Inclusions.

Changes may occur inside the inclusions after they were trapped, even if the inclusion volume remains constant. The temperature may change and give rise to phase changes or chemical reactions within the inclusion phases or with the inclusion walls. Solids may precipitate from dissolved species in the inclusion liquids, gases or vapors. Then, the measured characteristics may not be the same as the original ones.

The inclusion volume may change after inclusion trapping, and a chemical re-equilibration internally between phases or with the inclusion wall may take place after the change in temperature, pressure or volume. Solid, liquid and gas inclusions can readily migrate through crystals, and even metals, under the influence of strong thermal gradients (Shepherd et al., 1985). There is also evidence that the inclusions may leak, even from such sturdy materials as quartz, giving wrong information about the CO₂ content of the inclusions (Bakker and Jansen, 1990).

Inclusions formed after the host crystal has been formed are regarded as secondary inclusions. These are commonly formed in post-crystallization fractures initiated during mechanical or thermal stress. These cracks are later sealed, forming characteristic trails of secondary inclusions. Such inclusions are unrelated to and not representative of the original volatile environment during the growth of the host mineral. In a similar way, pseudosecondary inclusions may develop, but the fracturing and "healing" take place before the crystal growth has terminated. Pseudosecondary inclusions should reflect the volatile environment during the last growth stages of the host mineral, but not necessarily the initial stages of growth. These factors are not taken into account in the papers reporting recent studies of CO₂ in polar ice. Even such fundamental fact as the total disappearance of the air bubbles in deep ice (see below), which are used for paleoclimate reconstructions (e.g. Barnola et al., 1987), is not discussed or mentioned in these papers.

The upper, several tens meter deep part of the polar ice sheets is composed of porous snow and firn. Firn gradually changes into solid ice (at a depth between about 60 and 100 meters) in which the pores are occluded and form "air bubbles". Below about 900 to 1200 meters the air bubbles disappear in ice. In the ice cores recovered from deep bubble-free ice, the secondary gas cavities reappear, after relaxation of the load pressure. In these new secondary cavities the composition of gases cannot be the same as in the original air bubbles (Jaworowski et al., 1992). As the complete occlusion of the pores lasts from tens to thousands of years, depending on local conditions (e.g. precipitation rate), the air in the ice was assumed to be much younger than the ice (see e.g. IPCC, 1990). If this speculative assumption were correct, the air

in the firn should freely communicate with the atmosphere down to the firn–ice transition at about 60 to 100 meter depth, where the final occlusion occurs. However, in the polar firn there exists a dense, complex structure of impermeable ice crusts (see below) which precludes such free communication. The assumption was first proposed by Berner et al. (1980) and then elaborated by Schwander and Stauffer (1984). The latter authors supported this supposition by citing the results from ^{39}Ar dating of Greenland Ice (Loosli, 1983). However, the results in Loosli's (1983) paper indicate the opposite: at 70 m depth at Dye–3, Greenland, an ice core shows the age of the ^{39}Ar gas trapped in the bubbles to be ~70 years, i.e. the same as the age of ice, determined by the ^{35}Si method.

The assumption on the different age of air and ice was posed at a time when the concentrations of CO_2 were found to be similar for the air bubbles from the ice deposited in pre–industrial period and for the 20th century atmosphere (Delmas et al., 1980; Stauffer et al., 1981; Neftel et al., 1982; Neftel et al., 1983). For detailed discussion of the assumption on the different age of air and ice see Jaworowski et al. (1992).

The ice is not a rigid material. In the ice sheets the ice is constantly subjected to interaction with liquid water, gaseous/liquid/solid phase changes, recrystallization and plastic deformation. Pressure, temperature, and density of the ice are constantly changing, and compression and disappearance of air bubbles will occur. Secondary cavities are formed in the decompressed, bubble–free ice cores, together with macro– and micro–fractures. The gas in the secondary cavities and in the air bubbles communicate with the atmosphere through these fractures, which are successively "healed" by annealing.

In the very cold (below -50°C) firn strata the absorption of solar radiation leads to intense sublimation and melting of ice crystals, with a loss of H_2O mass. This leads to important structural, chemical and isotopic changes in the ice (see discussion in Jaworowski et al., 1992). Under these circumstances the ice neither behaves as a closed system nor as a rigid host material for air inclusions. No textural evidence has been presented that the original pseudosecondary inclusions have been preserved, and that no new secondary inclusions have been formed. We expect that the secondary inclusions dominate in deep ice core samples (the drilling may even destroy the integrity of the remaining original pseudosecondary inclusions present), and that their validity for the paleoatmospheric research may be questioned until such evidence exists. It is also known that ice at great depths in the ice sheets loses all its original air inclusions (see 5.1.5). This suggests that the gases diffused into the ice structure. This leads to problems connected with later release of these gases into secondary gas cavities reappearing in the relaxed ice cores, and makes it difficult to distinguish between air originally trapped in the ice structure and air occluded in the air bubbles.

The release of gases from inclusions in minerals is commonly achieved by decrepitation (e.g. Walder and Segalstad, 1987) or crushing (e.g. O'Reilly et al., 1990). The same methods have been used for inclusions in ice. The major differences between rock silicates and ice as a host mineral for the inclusions are the much lower melting point for ice and higher vapor pressures. The solubilities of gases in the H_2O phases are much higher than in, for instance, quartz. Furthermore, ice is physically not a very good container for the gaseous inclusions.

Free CO₂ is a very common major constituent of inclusions in a wide range of geological environments. On crushing a sample in the presence of liquid water or water vapor a large fraction of the CO₂ forms aqueous carbonic acid (Roedder, 1984). In glacier ice the measured CO₂ in the gas phase will not represent the total CO₂ in the gas inclusions, because much CO₂ will be dissolved in the (not analyzed) cold water, both present in the ice and produced at crushing. It seems that this has not been considered by Stauffer et al. (1981), when they described the "missing CO₂" during their ice melting runs. Barnola et al. (1987) reported that the presence of water vapor in inclusions gave low values for CO₂ when crushing the ice. They therefore added a flat "best estimate" of 5 ppm to the lower CO₂ concentrations found. Unfortunately the papers usually give no information on the CO₂/N₂/Ar ratios. Hence it is not possible to inspect the data as to the validity of their claimed atmospheric paleocompositions.

5.1.2 NITROGEN/OXYGEN/ARGON RATIOS

For estimation of the age of the air trapped in the upper 80 m of Antarctic and Greenland firn and ice Oeschger et al. (1985) assumed that "the entrapment of air in ice is essentially a mechanic process ... which occurs with no differentiation of the gas components". In support of this assumption they also stated that N₂/O₂/Ar ratios in ice are the same as in the ambient atmosphere. However, this assumption, which is crucial for age estimates, is not in agreement with the analytical results.

In the cold Antarctic environment at the Byrd Station (Antarctica), and at Camp Century (Greenland), Raynaud and Delmas (1977) found that the oxygen content in gas trapped in the ice was reduced by 0.83 – 1.2% in comparison with atmospheric air (i.e. an effect opposite to that expected from the solubility data; Hodgman et al., 1962; Weast et al., 1989) and enriched by 0.75 to 1.2% in argon. This is also opposite to the earlier findings of Scholander et al. (1961). In the firn samples from the Pionerskaya and Vostok stations in Antarctica Raynaud and Delmas (1977) found the concentrations of both these gases reduced in relation to nitrogen. The error of measurement of these gases was reported to be 0.5%. The authors stated that "par rapport a la composition atmospherique ... les effets observes sont donc faibles mais significatifs et indiquent un appauvrissement relatif des teneurs en O₂ et Ar". It is therefore difficult to understand why Oeschger et al. (1985) interpreted the Raynaud and Delmas (1977) finding as evidence that "N₂/O₂/Ar ratios in ice originating from very cold areas with no summer melting show that, within experimental uncertainty, the measured ratios agree with those in air". This statement Oeschger et al. (1985) used in support of an assumption that the gas trapped in the ice is about 100 years younger than the frozen water which encompasses it. However, the early data of the Oeschger group demonstrated that the Ar/O₂ ratio in various parts of a glacier may reach a value of 0.95%, which is much lower than the 1.19% in the ambient air (Berner et al., 1977). According to Berner et al. (1977), the Ar content in the ice (0.948%) is slightly higher than in the atmosphere (0.934%) and the O₂ content slightly lower (20.34% and 20.95%, respectively).

Stauffer et al. (1981) have measured the Ar/O_2 ratio in the old Greenland ice, but refrained from presenting the results. The value of this ratio was given by Stauffer et al. (1985) for ice samples from Dye-3 (Greenland) collected between 0 and 35 m depth. In these samples they found extremely high CO_2 concentrations, up to 28,000 ppm. In the surface layer the ratio of N_2/O_2 was 51.6 % (while being 26.8 % in the atmosphere), N_2/Ar was 2.6 % (1.19 % in atmosphere), and N_2/CO_2 was 4.4 % (0.042 % in atmosphere). This means that the entrapment of air in ice leads to a large differentiation of the gas components. The $\text{N}_2/\text{O}_2/\text{Ar}$ ratio in the glacier ice is of great importance for estimating the validity of this matrix for the studies of temporal changes of gases in the global atmosphere. The observed changes of this ratio in the ice mean that this matrix is not suitable for studying the original composition of the ancient atmosphere.

5.1.3 DEPLETION OF CO_2 IN SURFACE SNOW

An important finding of Raynaud and Delmas (1977) was the observation that in surface firn (up to 1 m depth) at the Pionerskaya and Vostok stations the concentration of CO_2 in the interstitial air was 160 to 240 ppm, respectively, whereas at that time in the atmospheric air this concentration was reported to be 310 ppm. This demonstrates that, even in snow that was not subject to longer firnification and firn-ice transition processes, the CO_2 content could have been reduced by up to 150 ppm, i.e. about 48% lower than in the ambient air of the same age. This important field experiment was never repeated in the later CO_2 studies.

The striking feature of the glacier data used as an evidence for a recent man-made CO_2 increase is that all of them are from ice deposited not in the last decades but in the 19th century or earlier. In these studies no information was presented on the recent concentrations of CO_2 in firn and ice deposited in the 20th century. The results of CO_2 determination in the pre-industrial ice are not compared with the CO_2 content in recently deposited snow, firn or ice but with its current levels in the atmosphere. To justify such comparisons an assumption was needed that the entrapment of air in ice is purely a mechanical process, involving no chemical differentiation of gases. However, as appears from the discussion in this report, and as was demonstrated by Jaworowski et al. (1992), this assumption is wrong.

5.1.4 EFFECT OF CARBONATES

In 13 samples (of Holocene and Wisconsin age) from an ice core from Camp Century (Greenland) Raynaud and Delmas (1977) found an average CO_2 concentration of 3500 ppm, and an average CO_2 concentration of 1300 ppm in a core from Vostok (Antarctica). These values were determined in whole samples of ice, and not only in the air bubbles. The authors added some drops of sulfuric acid to the ice before melting it. This probably added CO_2 to the original gas composition, by reactions of acid with carbonates present in the samples. Sulfuric acid and sulfates are commonly present in the polar ice. They

may possibly react with carbonates *in situ*, as well as after sampling of the cores of old ice. This may lead to a wide range of CO₂ values, as found in many studies of these cores. Delmas et al. (1980) suggested that the presence of carbonates in the ice may influence the CO₂ measurements.

High concentration of dissolved organic carbon (up to 0.32 mg per kg) was found in the Greenland snow by Twickler et al. (1986). These authors noticed that, in contrast to oxygen, the diffusion of CO₂ in the ice was measurable. This could change the original concentration of this gas in the air inclusions.

5.1.5 CHANGES OF AIR INCLUSIONS IN ICE

Stauffer et al. (1984) supposed that 20% of the observed temporal changes in CO₂ content in air inclusions ("bubbles") is due to enrichment in microbubbles. In the interpretation of their results from the Dye-3 (Greenland) core they assumed a 40 ppm surplus CO₂ from the microbubbles, and subtracted it from the measured values. Without this subtraction, the CO₂ level which they found in the approximately 30,000 – 40,000 year old ice was about 340 ppm, which is similar to the CO₂ content of the present atmosphere.

In polar glaciers, notably in Antarctica, air bubbles migrate and form inclusion clusters leaving outcrops of bubble-free ice that are several hundred meter long. It seems that gas inclusions migrate from less to more bubbly areas (Stehle, 1967). Migration of bubbles was also reported by Maeno (1967). At the Byrd Station (Antarctica) shrinkage of bubbles with increasing depth was observed to be faster below 800 m than expected from hydrostatic pressure; at a depth of 1100 m or more, no bubbles were visible. After several months storage of ice cores, bubbles started to form due to decompression (Gow and Williamson, 1975). Maeno (1967) also observed disappearance of air bubbles in the ice, which he interpreted as due to dissolution of air molecules into ice or due to mass transportation through diffusion of some kind of defects in the ice crystal. Both dissolution and diffusion are quite probable in the open-lattice configuration of an ice crystal (Maeno and Kuroiva, 1967).

The internal pressure in air bubbles trapped in ice ranges from 2 to 20 atmospheres (Scholander and Nutt, 1960). Langway (1958) found that, in the ice from a deep core in Greenland, the initial pressures of more than 13 atmospheres relaxed after a year's storage, a period shorter than usually encountered in glacier core studies. Such high internal pressures may influence the diffusion of CO₂ in the ice *in situ* and in the cores, and facilitate the creation of clathrates (hydrates) of gases in the intercrystalline liquid. Cracking of ice occurs due to the sheeting phenomenon caused by relaxation of the geostress when the ice cores are removed from deep layers (for detailed discussion see Jaworowski et al., 1992). Pressurized gases may then escape from the bubbles through microcracks.

The air bubbles collected from ice by the dry extraction technique contain half or less of CO₂ present in the ice. This low concentration, and not the content in the whole ice sample, is taken into account in the estimates of the CO₂ level in the pre-industrial atmosphere (see Chapter 5.2).

A striking illustration of the effects of glacial processes on the CO₂ content in ice, recovered from great depths is presented in Figure 5. The air and CO₂ content fluctuations in the ice are more or less parallel between ~900 and 1130 m depth. But below this depth a dramatic decrease in the CO₂ concentration was found, not accompanied by a similar decrease in air content (Berner et al., 1980). At corresponding depths all air bubbles disappear in the ice.

The total disappearance of air bubbles was observed by Gow and Williamson (1975) at the Byrd Station (Antarctica) in ice from depths below 1100 meters. The authors found that air was present in the bubble-free ice, as after decompression of the ice core during storage, the secondary gas cavities were formed again. It is interesting to note that at Camp Century (Greenland) and the Byrd Station (Neftel et al., 1982) a decrease in CO₂ content also occurred at the depth where all original air bubbles disappear, i.e. at about 1200 m.

At a certain depth, when the gas pressure exceeds the dissociation pressure, the gas is converted to the clathrate hydrate (solid) form, provided that there is enough liquid H₂O. At the Byrd Station (Antarctica) this pressure is reached at a depth of 800 m (Miller, 1969). At Vostok the predicted depth is 400 m, however sporadic bubbles were observed below 800 m (Korotkevich et al., 1978). The dissociation pressure of the CO₂ clathrate is about 13 to 20 times, depending on temperature, lower than that of N₂ and O₂, and starts at about 5 bars below –15°C (Takenouchi and Kennedy, 1965; Miller, 1969, 1973). This means that at the same temperature the CO₂ clathrates will be formed at much shallower depth than clathrates of the major components of air. This phenomenon is a plausible cause for the decrease of the CO₂ concentration in ice below 70 meters, observed in Greenland and Antarctic cores by Berner et al. (1980), Neftel et al. (1982), Neftel et al. (1985), Raynaud and Barnola (1985) and Wahlen et al. (1991).

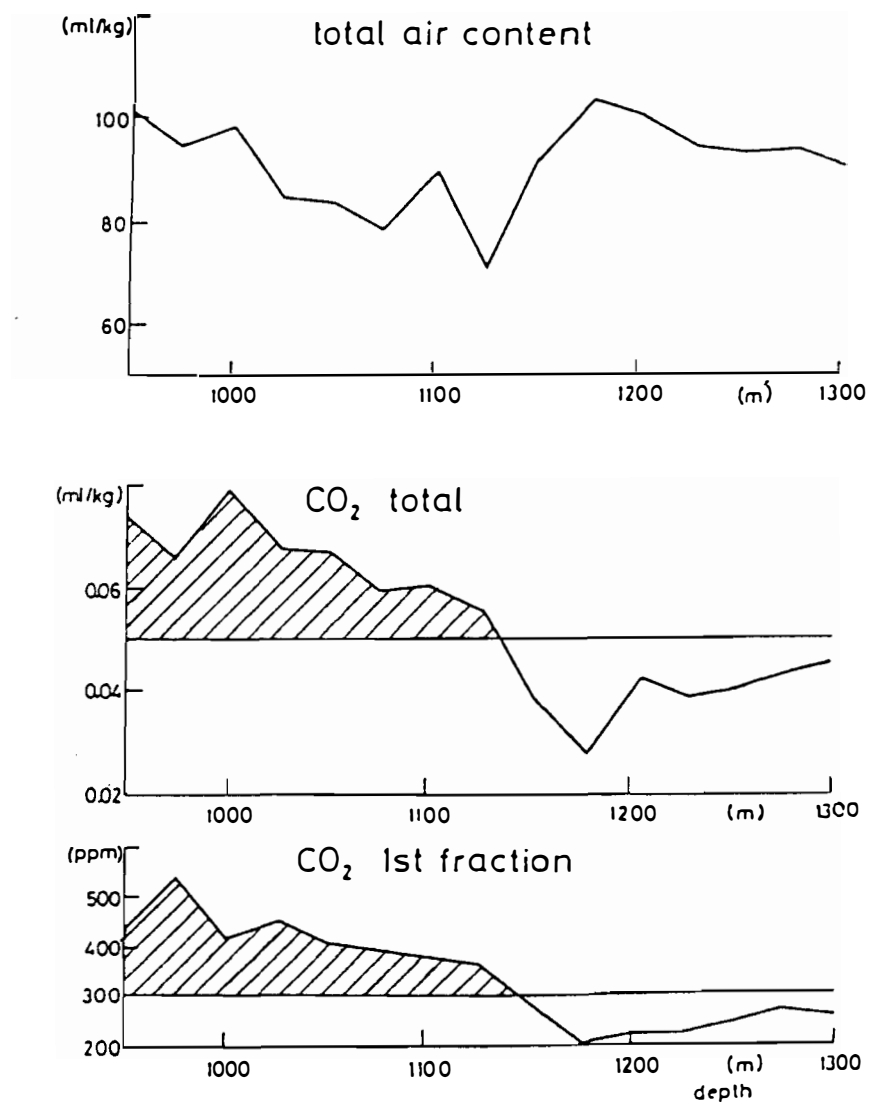


Figure 5. Changes of air and CO₂ content in glacier ice from Camp Century (Greenland) versus depth (after Berner et al., 1980). Note the decrease in CO₂ content below ~1130 m, where air bubbles were reported to disappear.

Spacial fractionation of gases may occur due to selective formation of clathrates and different solubilities of the different air gases. This is coupled with the migration of liquids in the extensive capillary network of the glaciers. After decompression of the cores the different components of air reenter the gaseous phase at different rates, forming new secondary air bubbles. At low temperature at this stage more CO₂ may remain in solution than other gases, due the higher retrograde solubility of CO₂ (≥ 74 , ≥ 35 , and ≥ 31 times higher solubility than that of N₂, O₂, and Ar, respectively, on an equal molar basis) whereas most of the other air constituents enter the secondary air bubble. The dissociation pressure depends on the temperature. At greater depths in the polar ice caps, where temperature rises, one may expect release of gases from the clathrates. However, the clathrates remain stable because the pressure increases. The gases remaining in solids will be subject to diffusion and chemical processes. They may migrate in the intercrystalline liquid for a time sufficient to change their original composition. After release of the geostress the clathrates will dissociate in the recovered cores, at various rates, depending on the differences between the original temperature and pressure *in situ* and during storage.

A sudden decrease in the CO₂ concentration from 250 to 180 ppm occurred in the Vostok core at a depth of 400 m (Barnola et al., 1987). Such a depth can be predicted for this location for conversion of CO₂ to the clathrate form (Takenouchi and Kennedy, 1965; Miller, 1969). The CO₂ decrease was associated with drastic structural and other physical changes in the ice, occurring both *in situ* and in the core (Jaworowski et al., 1992).

5.1.6 ICE LAYERS

The ice layers can not only change the chemical composition of the gases in the ice, but they are also important impermeable barriers for the penetration of gases from the atmosphere into the deeper layers of firn. In Antarctica such impermeable layers were observed and extensively studied down to a depth of more than 100 m (Kotlyakov, 1961; Gow, 1968, Watanabe, 1977; Korotkevich et al., 1978; Repp, 1978; Neftel et al., 1985; Raynaud and Barnola, 1985). The processes leading to formation of ice crusts in extremely cold Antarctic ice sheets, due to absorption of solar radiation, are described by Gow (1968) and reviewed by Jaworowski et al. (1992). Raynaud and Barnola (1985) stated that air in the Antarctic firn cannot be well mixed with the atmosphere due to the existence of these impermeable layers which isolate the air in the firn from the free atmosphere even at shallower depth. It is therefore astonishing that the assumption that air bubbles (with the same concentration of CO₂ as in 1983 atmosphere) in ice from a depth of more than about 70 m, deposited in the 19th century could represent the composition of the 1983 atmosphere (Neftel et al., 1985) was so credulously accepted. In this assumption, which is based on an observation that the air pores became closed at a depth of 70 m and on porosity measurements (Berner et al., 1978; Schwander and Stauffer, 1984), the sealing effect of the impermeable layers was not taken into account, even though such layers were observed by CO₂ students (e.g., Neftel et al., 1985) and extensively studied by others. The

physical and chemical processes which may change the original composition of atmospheric air along its long migration route in porous material to such a depth were also neglected.

5.1.7 EFFECTS OF DRILLING

Drilling the ice cores is an extremely brutal procedure, which leads to important changes in the structure and composition of ice. As discussed by Jaworowski et al. (1992) in the very moment of drilling the a dense cracking of ice occurs due to the sheeting phenomenon, caused by rapid decompression of the load pressure in the ice. In all ice cores from below a depth of 100 meters a dense stratification of horizontal macro- and micro-cracks occurs. The visible, macro-crack strata appear at about 2 to 5 mm intervals. Through these fractures the drilling fluid (a mixture of diesel oil or kerosene and trichlorethylene), highly contaminated with heavy metals, acids, and particulates, penetrates deeply into ice, during recovery of the cores from the boreholes. At the surface the macro-cracks are soon "healed" by annealing, sealing the contaminants inside the cores. The "healed" fractures are clearly visible even in cores stored for many years in freeze-rooms. Extremely high degree of contamination of cores of ancient polar snow, with hundred of thousand times higher element concentrations than in the surface snow, were often reported, including cores from Camp Century (Greenland), Vostok, and Byrd Station (Antarctica), which are regarded as classic cores for CO₂ and isotopic studies (Ng and Patterson, 1981; Neftel et al., 1982; Kudryashov et al., 1984 a and b; Petit et al., 1990). Cracking and contamination can lead to dramatic changes in the chemical and isotopic composition of the ice. These effects are discussed in detail by Jaworowski et al. (1992).

5.1.8 CONCLUSIONS

The physical phenomena discussed above, and chemical reactions between CO₂ and chemical species dissolved in the intercrystalline liquid, must change the proportion of gases in the secondary air inclusions (trapped in fractures and between ice crystals), as well as in the primary inclusions (gases originally dissolved in water, trapped when the water froze to ice), pseudosecondary gas inclusions (trapped in pores between the ice crystals, and in the "air bubbles"), and in secondary gas cavities (formed after the decompression of cores), compared to the original atmospheric composition. Therefore, the concentrations of gas species (like CO₂) determined in the air bubbles and secondary gas cavities from Greenland and Antarctic cores, e.g. from the Vostok core (Barnola et al., 1987), cannot be regarded as representing original atmospheric concentrations of gas species in the ancient atmosphere.

5.2 MEASURED CO₂ LEVELS IN GLACIER ICE

The majority of early CO₂ measurements were made by melting ice samples weighing up to several kilograms, from which CO₂ was extracted after the ice was melted and resulting water boiled. Later, smaller samples (usually ~300 g) were used, and extraction was carried out first during a short time, 7 – 15 minutes, before ice had completely melted. The second extraction was carried out during several hours. The first fraction was interpreted as representing CO₂ contained in the air bubbles trapped in the ice. The second fraction was believed to represent the total content of this gas in the ice. The "dry" extraction of CO₂ from air bubbles by shaving the ice samples in a closed container was used in the very first CO₂ studies in ice as well as the microanalysis of CO₂ in single air bubbles in ice (Coachman et al., 1956). Since 1980 a method consisting of crushing the ice samples in low temperature, was introduced (Delmas et al., 1980). With this method the gas was supposed to be extracted only from the air bubbles, and the weight of samples used by various authors ranged from 1 to 1400 g.

The early determinations of CO₂ in melted ice samples produced a very wide range of results, with peak values reaching several thousands ppm, found after several hours of extraction (i.e. in the total volume of gas contained in the ice structure). The short-term extraction (up to 15 minutes) from melted samples, and crushing the small cubes of ice, produced much lower results (i.e. less than half of total volume results).

We are aware of only one study carried out on snow cores sealed at the moment of collecting. All other cores were stored unprotected during up to 16 years before analysis. In the sealed snow cores Raynaud and Delmas (1977) demonstrated that CO₂ concentration in the air trapped in the near surface snow at very cold Vostok and Pionerskaya sites (Antarctica) was up to about 50% lower than in the atmosphere (Table 2).

The first determinations carried out at a temperate Norwegian glacier showed rather high concentrations of CO₂ in the ice, similar to those found later on polar ice caps. On the Greenland ice cap Scholander et al. (1961) found CO₂ air concentrations ranging from about 100 to 900 ppm in 20 samples of approximately 2700 years old ice (Murozumi et al. 1969). Old ice samples from other localities in this region had CO₂ concentrations from a few ppm to more than 1500 ppm. Scholander et al. (1961) found large differences between the chemical composition of single air bubbles from the same ice samples. This suggests that, when using small samples with a mass near one gram containing few air bubbles, the analytic uncertainty is increased.

In an Antarctic ice core Matsuo and Miyake (1966) found a CO₂ concentration range of 280 to 2900 ppm. Raynaud and Delmas (1967) measured CO₂ concentrations ranging between 1700 and 7400 ppm in a 108.5 to 1345 m deep ice core from Camp Century, Greenland, and between 900 ppm and 1800 ppm in a 71 to 300 m deep core from Byrd Station, Antarctica.

Delmas et al. (1980) found high concentrations of CO₂ in ice from two Antarctic cores. At a depth between 113 and 670 m the concentrations ranged from 210 to 740 (average 440) ppm in gas from the melted samples. These values were determined not in the original ice samples, in which the authors found

concentrations an order of magnitude higher (1050 to 6100 ppm), but in samples that were "copiously" rinsed with water or ethylalcohol. This procedure, which might change the original chemical composition of the samples, was used because the authors supposed that the carbonates present in the sample might have influenced the CO₂ readings.

From the same ice cores Delmas et al. (1980) released about 75% of the gas by pulverization of the frozen "dry" samples. In 22 samples from one core, at various depths between 37 and 893 m, they found CO₂ concentrations randomly ranging between 160 and 360 ppm. In a second core, in 13 samples from various depths between 37 and 301 m, they found concentrations ranging between 160 and 350 ppm. The lowest values were measured in the cracked parts of the core, which "lost important volumes of gases". In both cores exactly the same average concentration of 250 ppm CO₂ was calculated.

Very high concentrations of CO₂ ranging between about 300 and 2350 ppm were found by Neftel et al. (1982) in the air bubbles in several hundred year old ice from a Dye-3 core in southern Greenland. At Camp Century in another region of Greenland, they found CO₂ concentrations ranging from about 140 to 470 ppm in several hundred to 40,000 years old ice. At the Byrd Station (Antarctica) in ice of similar age they found CO₂ concentrations ranging between about 100 and 500 ppm. They stated that only the lowest values (which they fail to specify) "best represent the CO₂ concentrations of the originally trapped air", and assumed that the higher readings were due to contamination of the samples with a mixture of diesel oil and trichlorethylene, used as a drilling fluid, which penetrated the cracks in the core. But they did not discuss the possibility that the low readings might be due to the same sampling artifacts. From this description, the cores sampled with such a technique should not be qualified for CO₂ determinations.

In a very cold region at the North Central Station (Greenland) Neftel et al. (1982) found in 22 samples from a 13-cm-long part of core from a depth of 103 m a low average CO₂ value of 271 ppm (the detailed results and range not presented). This value is much lower than in ice samples from another cold region in Greenland (Camp Century), covering a period between 500 and 5000 years ago. In these latter samples CO₂ concentration ranged up to about 440 ppm, with the average of about 380 ppm. However, the low value of 271 ppm, which is from a 13 cm long core, and not an average from all determinations in Greenland (which is similar to, or higher, than the present atmospheric level) is often used in climatological estimates as representative for the pre-industrial period (e.g. Schneider, 1989).

Raynaud and Barnola (1985) measured the CO₂ concentrations in air bubbles from a core collected at the D57 Site in Antarctica. The ice was sampled from the core at various depths below 89 m. The measured annual snow accumulation rate at this region, upslope the sampling site, ranged between 4.4 and 45 cm of ice equivalents. The authors do not report the age of the ice, which, however, can be calculated from the assumed accumulation rate values. The accumulation rate of 45 cm per year corresponds to an ice age of about 1849 A.D. at the depth of about 89 m, and 1622 A.D. at the depth of about 197 m. The authors were aware of the occurrence of impermeable layers, and therefore it is not clear from the presented evidence why they assigned an age of 1940 A.D. for the air bubbles in ice from a depth of 89 m, and 1560 A.D. from

197 m depth. They stated, however, that the age of bubbles "may be, in fact, older by several tens of years ... because the air can be isolated" (with impermeable ice layers).

In the air bubbles preserved in the ice from 89 m depth Raynaud and Barnola (1985) found an average CO₂ concentration of 288 ppm, and in the ice from 197 m depth a concentration of 271 ppm. They interpreted the 17 ppmv change as demonstrating an anthropogenic increase of CO₂ in the atmosphere. The authors did not account for a loss of CO₂ from the bubbles due to diffusion in intercrystalline liquids, and due to numerous other factors discussed in Chapter 5.1.5.

The obvious drawback of the Raynaud and Barnola (1985) paper is a lack of data from the first few meter depth of firn, which would serve as a contemporary reference. As discussed in Chapter 5.1.3, in the 1 m thick layer of surface firn in Antarctica, the recorded concentrations of CO₂ were up to ~50% lower than in the atmospheric air at the same time. No statistical evaluation of the temporal trend of data was presented. The authors compared their results with the current Mauna Loa atmospheric measurements, and stated that their results "indicate clearly the increase in atmospheric CO₂ due to burning of fossil fuels, and probably also due to the anthropogenic influence on the biosphere over the nineteenth and twentieth centuries". This conclusion is not consistent with the presented results, which probably represent a random fluctuation of CO₂ concentrations in the ice, due to natural physical and chemical processes at the snow/air interface in the atmosphere and in glaciers. From the difference of 17 ppm between the mean CO₂ concentration of 288 ppm (st. dev. 6.3) and 271 ppm (st. dev. 8.5); recorded in ice from 89 m and 197 m depth, respectively, it is not possible to judge if this difference is significant. Raynaud and Barnola (1985) were unable to support by any factual evidence their assumption that some of their air samples were from the twentieth century.

Similar flaws in estimation of the age of air in the bubbles, neglecting the enrichment and depletion processes in snow and ice, lack of analysis of near-surface layers, and not accounting for exchange between CO₂ in the air bubbles and in the ice itself, can be found in the Neftel et al. (1985), Pearman et al. (1986), Barnola et al., 1987 and Wahlen et al. (1991) papers. Neftel et al. (1985) measured the CO₂ content in air bubbles from an ice core collected in 1983 at the Siple Station, Antarctica. The accumulation rate at that site was about 50 cm (water equivalent) per year. At a depth of 7 m they found a 2 to 10 mm thick impermeable ice layer formed from melt water. They also noted that at a depth between about 68 and 69 m two impermeable layers occur. At this depth, corresponding to an ice age of 1891 A.D., they found an average CO₂ concentration of 328 ppm (range not indicated), and interpreted this as an evidence of an effect of fossil fuel burning in the 20th century.

Neftel et al. (1985) assumed that in the ice deposited about 1891 A.D. the air was trapped between 1962 and 1983 A.D. They did not measure the age of air. Among arguments in support of this speculative assumption, they used a value of the CO₂ concentration in the ice from 1891 A.D. of 328 ppmv which was the same as measured in the South Pole atmosphere in 1973/74. This seems to be circular logic. The coincidence simply indicates that in 1891 the atmospheric CO₂ level was the same as in 1974.

Neftel et al. (1985) concluded that around 1750 A.D. the atmospheric concentration was 280 ppm, and has increased since, because of human factors, by 22.5% to 345 ppm in 1984. This conclusion is based on a speculative assumption of the age of air trapped in the ice, on circular logic, and neglecting the physical and chemical processes in the ice sheets and artifacts in the decompressed and contaminated ice cores.

The Siple core is treated as a classical proof that the pre-industrial CO₂ concentration in the atmosphere was about 70 ppmv lower than now (e.g. IPCC, 1990). One should note, however, that this core was exposed to post-coring melting. The melting, which must have caused important changes in the gaseous composition, was not reported by Neftel et al. (1985) (see discussion in Jaworowski et al., 1992). The data from this core were adjusted to overlay exactly the recent atmospheric concentrations at Mauna Loa (Siegenthaler and Oeschger, 1987). A figure demonstrating this adjustment is reproduced in countless publications (e.g. in IPCC, 1990). The overlaying was achieved by assuming that the age of the trapped air was 95 years younger than the ice. Without this speculative assumption the Mauna Loa and Siple data do not agree at all. As was indicated by Jaworowski et al. (1992), rather than representing the past atmospheric changes, the results show how the CO₂ concentrations in the Siple core decrease with the increasing load pressure up to about 15 bars, due to clathrate formation, differential dissolution of gases in the intercrystalline liquid brine, and other processes in the ice sheet and in the ice core.

Ice cores can be easily contaminated by ambient air during field work (Loosli, 1983). This contribution can reach 36 to 100%, as indicated by the measurements of ⁸⁵Kr and ³⁹Ar, radioactive gas isotopes produced in nuclear explosions and reactors and by cosmic radiation. This suggests that other ambient gases, including CO₂, may contaminate the ice cores during field work and storage, and that there exist opened routes through which the gases can escape from the ice cores. Oeschger (1989) presented a photograph showing handling of an ice core used for CO₂ studies in the presence of persons smoking cigarettes. This indicates that the contamination problems are not seriously considered in gas analysis of ice cores. Under such circumstances ice is exposed to higher than ambient CO₂ air concentration, which could change the original composition of the ice core samples. This possibility was noted by Alder et al. (1969) and Stauffer et al. (1981) who noticed "that ice, and especially firn, samples in contact with an atmosphere enriched in CO₂ get contaminated".

It is interesting to note that Raynaud and Barnola (1985) found CO₂ concentrations in ice lower than that of the present atmosphere, while Neftel et al. (1985) found CO₂ concentrations in ice similar to that of the present atmosphere. However, both groups reached the same conclusion: that their results demonstrate an anthropogenic increase of atmospheric CO₂. This suggests that there exists a tendency of a unidirectional interpretation of analytical results.

TABLE 2. CONCENTRATIONS OF CO₂ IN GLACIER ICE (ppm by volume).

Age of ice	Locality	Concentration	Reference
PI ³	Storbreen ⁶ (Norway)	~200–2900	Coachman et al., 1956 Coachman et al., 1958 a
	Greenland		Coachman et al., 1958 b
PI	11 localities	~100–2500	Scholander et al., 1961
2700 BP ⁴	Tuto Tunnel	~100–800	Scholander et al., 1961
PI	Antarctica	280–2900	Matsuo and Miyake, 1966
Holocene and Wisconsin	Greenland	1700–7400	Raynaud and Delmas, 1977
	Antarctica		Raynaud and Delmas, 1977
>100 BP	Byrd Station	900–1800	
Few years BP	Pionerskaya ⁶	160	
Few years BP	Vostok ⁶	240	
180 BP	Greenland	400–1200	Berner et al., 1978
PI	Antarctica whole ice ⁵ air bubbles ⁶	210–740 160–335	Delmas et al., 1980
PI up to 40,000 BP	Greenland Antarctica	200–800 230–400	Berner et al., 1980
5000–30,000 BP	Greenland	200–700	Stauffer et al., 1981

³ PI pre-industrial, exact age not given.

⁴ Years before present.

⁵ Samples washed in water or alcohol.

⁶ In gas inclusions after dry extraction, otherwise in melted ice.

TABLE 2 – continued.

Age of Ice	Location	Concentration	Reference
180 BP	Greenland	250–1000	Stauffer et al., 1981
180 BP	Greenland ⁶	300–550	Stauffer et al., 1981
1000?–30,000 BP	Antarctica	200–520	Stauffer et al., 1981
>100 BP 600–40,000 BP ~680 BP	Greenland		
	Dye-3 ⁶	300–2350	Neftel et al., 1982
	Camp Century ⁶	140–470	Neftel et al., 1982
	North Central ^{6,7}	271	Neftel et al., 1982
600–40,000 BP	Antarctica		
	Byrd Station ⁶	100–500	Neftel et al., 1982
30,000–40,000 BP	Greenland		
	Dye-3 ⁶	135–275	Stauffer et al., 1984
>~300 BP	Antarctica		
	D57 ⁶	247–295	Raynaud and Barnola, 1985
1663–1891 AD 110–820 BP	Antarctica		
	Siple ⁶	279–328	Neftel et al., 1985
	South Pole ⁶	278–281	Neftel et al., 1985
1530–1900 AD	Antarctica		
	Law Dome ⁶	268–326	Pearman et al., 1986
4050–163,670 BP ⁶	Antarctica		
	Vostok	191–296	Barnola et al., 1987
1310–1720 AD	Greenland		
	GISP 2	272–310	Wahlen et al., 1991

⁷ In one 11 cm thick layer at 103 m depth.

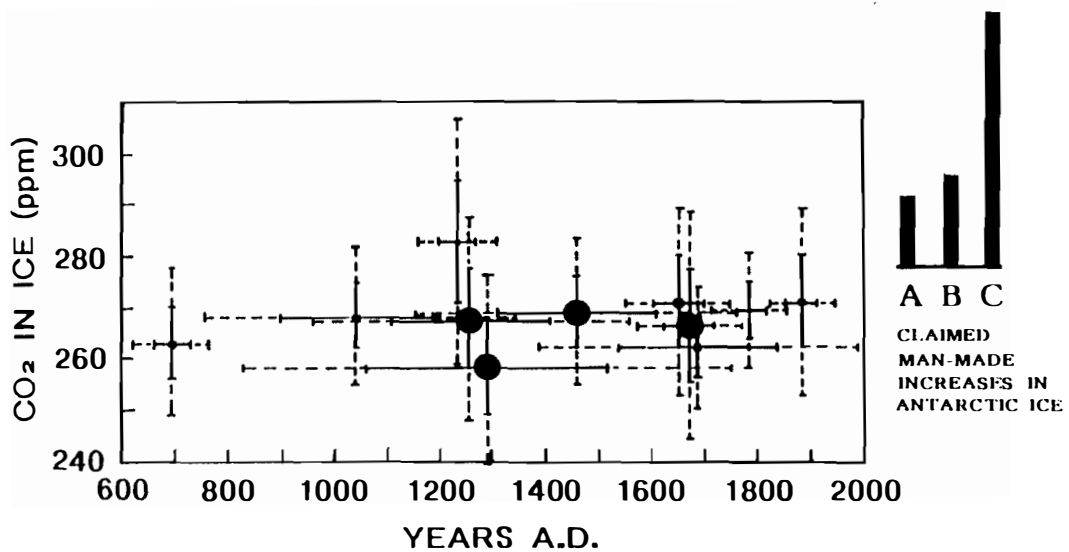


Figure 6. Errors of CO₂ measurement in air bubbles in ice cores from Greenland and Antarctica (modified after Oeschger et al., 1985) and claimed reported increases in CO₂ levels in recent ice samples due to fossil fuel burning (A: Pearman et al., 1986; B: Raynaud and Barnola, 1985; C: Neftel et al., 1985). Solid line indicates ± 1 standard deviation (assumed to include ~68% of the observations), broken line indicates ± 2 standard deviations (assumed to include ~95% of the observations).

An example of an unusual selection of results is a paper by Pearman et al. (1986). The authors collected 74 ice samples from an Antarctic ice core, from which they rejected 32, because the CO₂ concentrations differed by more than 7 ppm from "at least one other sample of comparable age". They stated that between 1850 and 1900 an increase in CO₂ concentration of 13 ppm occurred, and that this corresponds to a net global CO₂ input of 48 GT, which cannot be explained by the small amount of fossil fuel consumed during this period.

Finally, one should compare the range of analytical uncertainty with the temporal differences in CO₂ concentration in ice used recently to demonstrate the atmospheric increase of this gas. Such temporal difference in the case of Raynaud and Barnola (1985) was 17 ppm, in the case of Neftel et al. (1985) 49 ppm, and in the case of Pearman et al. (1986) 13 ppm. According to Oeschger et al. (1985) the "errors" (at an assumed 68% probability level) of the measurements of CO₂ in air trapped in ice cores from Greenland and Antarctica range between 11 and 24 ppm. At an assumed 95% probability level the "errors" reach about 47 ppm. It is clear from these considerations that the claims of a recent increase in atmospheric CO₂ content, found in the glacier gas inclusions, is based on rather spurious evidence. The "errors" of measurements at a 95% probability level are larger than or close to the claimed rise in atmospheric CO₂ (see Figure 6).

Classical examples of CO₂ measurements in the Greenland and Antarctic ice are given in Figures 7 and 8. These measurements show typical long-term (6000 to 30,000 years B.P.) random variations between 200 and 700 ppm (Figure 7), and short-term random variations in a 90 cm long core of 180 years old ice, of between ~280 and 1000 ppm (Figure 8). It would be difficult to believe that these variations represent the real changes in CO₂ levels in the atmospheric air. Rather, they resulted from the physical and chemical processes in the glacier ice, or are due to artifacts during sampling and analyses of the ice. As may be seen in Figures 5 and 6, after a 15 minutes extraction the concentration of CO₂ recovered from the melted ice was much lower than after a 7 hour extraction. N₂, O₂ and Ar do not reveal such behavior. Only ~50% of the CO₂ is extracted after the melting process is terminated. Many hours are needed in order to make the extraction complete. Dry extraction by crushing the frozen samples releases the air contained in bubbles but does not allow measurements of the total CO₂ content (Stauffer et al., 1981).

Stauffer et al. (1981) rather incorrectly assumed that, in spite of these difficulties, the CO₂ concentrations measured in the air released from the ice, after 15 minutes extraction, represent the atmospheric content with an accuracy of 22 ppm. With this inappropriate method glaciological studies provided the first confirmation of the Callendar (1958) value of 292 ppm CO₂ level for the 19th century atmosphere. However, the "wet extraction" studies also provided valuable information. It was demonstrated that the ice itself is not CO₂-free. Depending on conditions changing both in the ice sheets and in the cores, ice rich in CO₂ may be either a source or a sink for the CO₂ trapped in the air bubbles.

The concentrations of CO₂ in air recovered from ice with the dry gas extraction method ranged between 140 and 2350 ppm (Table 2). As was demonstrated by Jaworowski et al. (1992) these data represent the effects of about twenty physical and chemical processes occurring in the ice sheets and in the ice cores,

rather than the original atmospheric concentrations. The value of 280 ppm, widely accepted on the basis of glacier studies as the pre-industrial atmospheric CO₂ level, apparently results from such processes, invalid assumptions and arbitrary rejection of high readings.

We are not discussing the validity of analytical methods used in the current CO₂ studies in glaciers. We criticize the quality of ice as a closed system, which is an absolutely essential criterion for its use to reconstruct the composition of the pre-industrial atmosphere. We also criticize the methodology of sampling, and biased interpretation of results. Ice is neither a rigid material, nor may be regarded as a closed system, suitable for preserving the original chemical and isotopic composition of atmospheric gas inclusions. Ice core drilling is an extremely brutal procedure leading to drastic changes in the ice samples, precluding their reliability for gas analyses. The concentrations reported from the pre-industrial ice, no matter whether they were higher, equal to, or lower than the present atmosphere, were always interpreted as indicating an anthropogenic increase of atmospheric CO₂. In this interpretation differentiation processes in the ice were neglected or downplayed. In fact they were never thoroughly studied, and this is one of the reasons why the glaciological studies were not able to provide a reliable reconstruction of the CO₂ level in pre-industrial and ancient atmospheres.

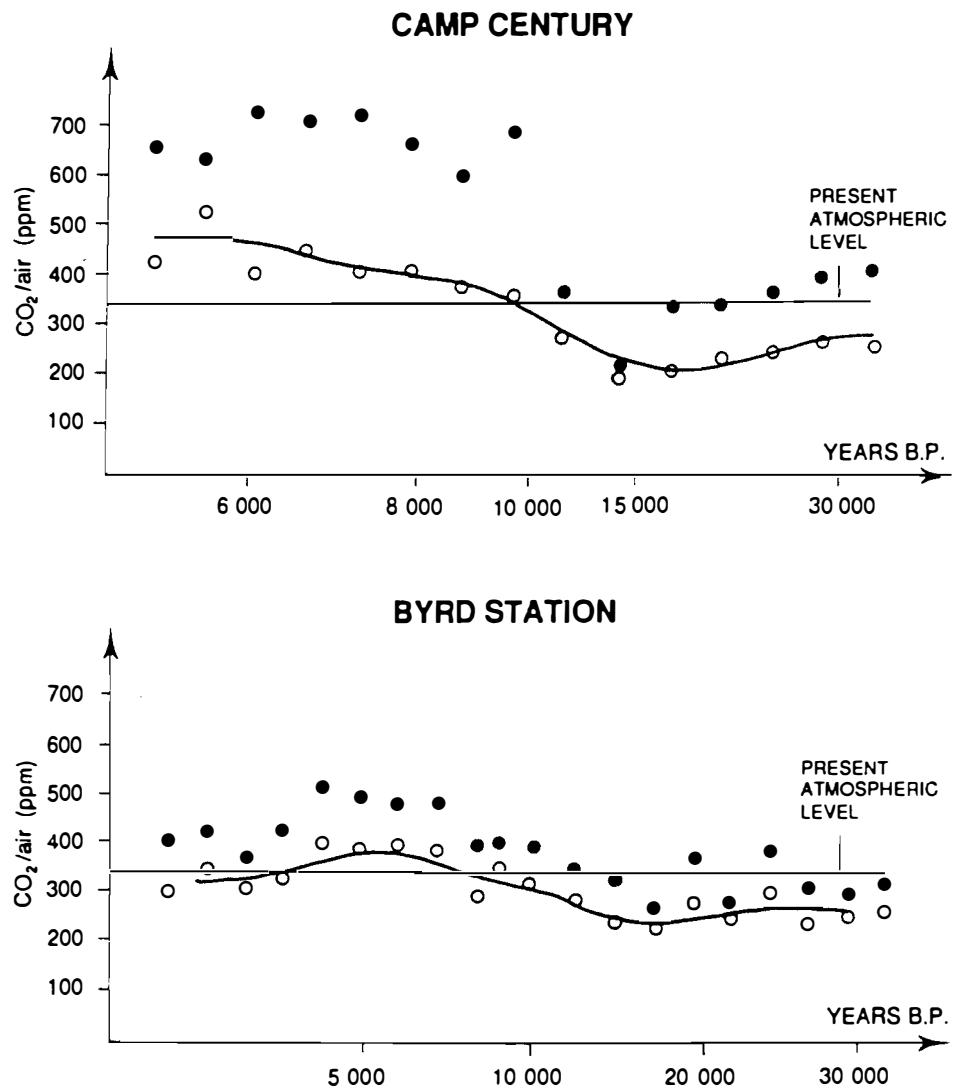


Figure 7. Concentrations of CO₂ in air from the Camp Century (Greenland) and the Byrd Station (Antarctica) ice cores. White dots represent CO₂ concentrations after 15 minutes extraction, black dots after 7 hour extraction. After Stauffer et al., 1981.

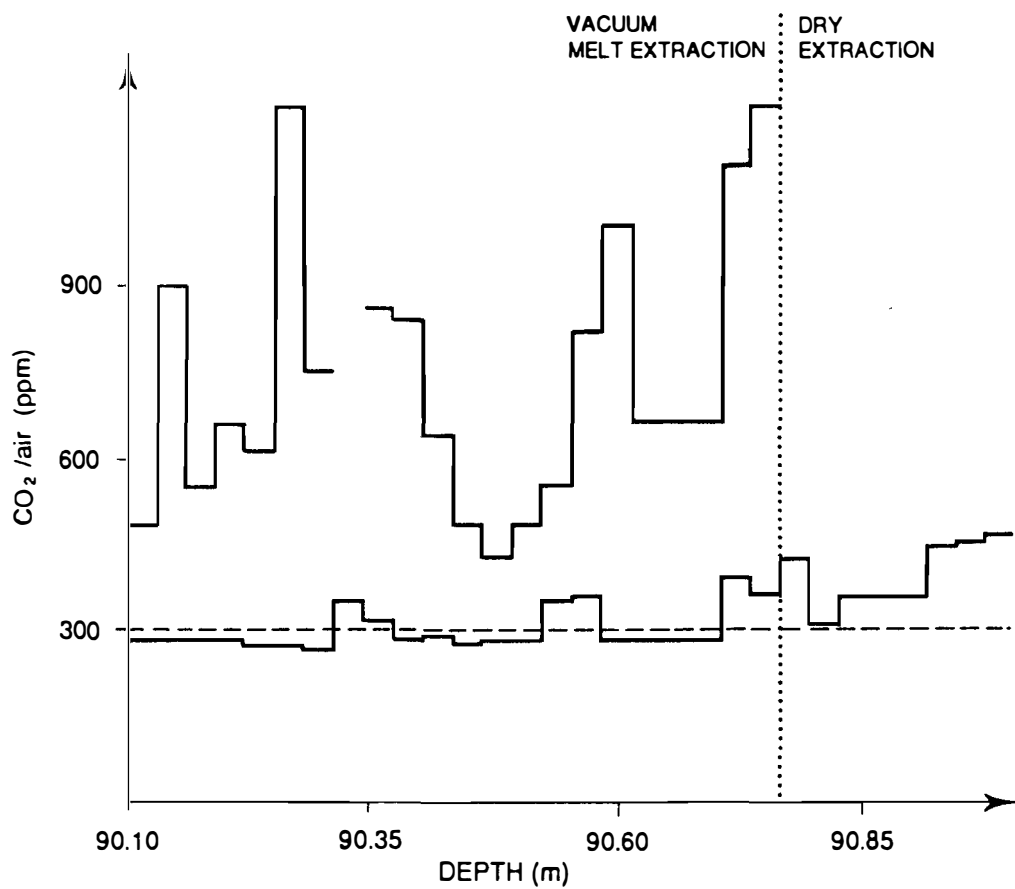


Figure 8. Concentration of CO₂ in a 90 cm long piece of the Camp Century (Greenland) ice core. The lower curve represents the values after 15 minutes extraction from melted ice, and the results after dry extraction. The upper curve shows the CO₂ content after 7 hours extraction. After Stauffer et al., 1981.

5.3. CONCLUSIONS

- (1) The results of CO₂ measurements in air bubbles in pre-industrial ice ranged between 140 and 550 ppm. In ice from the 19th century and before, these concentrations were found to be either the same, or considerably higher or lower than the present atmospheric levels. The "errors" of measurements at a 95% probability level are larger than or close to the claimed rise in atmospheric CO₂. Hence a rise, fall, or steady level of CO₂ in the atmosphere cannot be established from the available CO₂ gas inclusion data. The value of about 290 ppm, often accepted as representing the average global concentration of CO₂ in the pre-industrial atmosphere, is highly uncertain and speculative.
- (2) Even the recent snow deposits do not represent the original CO₂ level in the atmosphere. Air trapped in near surface Antarctic snow has about 50% lower CO₂ content than the ambient atmosphere.
- (3) Chemical and physical processes during the early atmospheric history of the snow crystals, and in the glacier firn and ice, can both decrease or increase the CO₂ content in air trapped in the ice, relative to the original atmospheric concentration. Probably the most important cause of these changes is the presence of liquid in snow and ice, even at extremely low temperatures. Because of its retrograde solubility CO₂ easily dissolves in cold water and in concentrated acid brines from an intercrystalline capillary network. CO₂ may form solid clathrate. CO₂ may also migrate from the air bubbles into other gaseous inclusions in the solid ice. Other air components have different solubilities in water than CO₂, and different clathrate dissociation pressures. This leads to changes in the chemical and isotopic composition of gases trapped in ice.
- (4) Moreover the sampling and analytical methods used for CO₂ determination in glacier ice may change the original content of this gas in the samples, due to incomplete release of the gas, loss of CO₂, or due to contamination.
- (5) The establishment of the true pre-industrial level of CO₂ in the atmosphere is of great importance. However, the current polar ice sampling techniques are not able to provide a reliable material for reconstruction of the composition of the pre-industrial atmosphere. New methods for *in situ* air sampling from polar ice sheets should be developed, as suggested by Jaworowski et al. (1992).

6. HYDROGEN AND OXYGEN ISOTOPES IN GLACIERS

Hydrogen and oxygen stable isotope determinations have provided useful results in the field of glaciology (e.g. see Hoefs, 1980, and Amason, 1981, for references). For example, Epstein et al. (1965) used hydrogen and oxygen isotopes to find an average annual accumulation rate of 7 cm of water at the South Pole between 1958 and 1963, in good agreement with stratigraphic and radioactive dating results. The δD and $\delta^{18}O$ values are used for reconstruction of paleotemperatures and to date the snow and ice layers as a function of depth.

However, the isotopic composition of the snow can be changed by numerous factors, including snow drift (Arnason, 1981). The isotopic ratios for the light isotopes in snow and ice are changed considerably every time there is a phase change (between vapor/liquid/solid), especially at low temperatures, as a function of mass ratios involved in the phase change reaction (e.g. Hoefs, 1980). Kinetic isotope effects, common at low temperatures, may further change the original isotopic composition of precipitation, and lead to errors in calculations based only on equilibrium isotope effects.

The short-term fluctuations of δD and $\delta^{18}O$ have been ascribed to annual summer/winter layering and used for dating the ice and snow samples. These short-term peaks are gradually eliminated in old ice (Langway, 1967) and in upper parts of the ice sheets (Grootes et al., 1990). This is due to homogenization processes, such as sublimation, melting and refreezing of water percolating through snow, firn and ice, movement of water vapor along the temperature gradients, and plastic deformations (Faure, 1986). Thus, detailed comparisons between the isotope records of the ice sheets in Greenland and Antarctica are unreliable (Hoefs, 1980). Arnason (1981) gives examples of isotope variations in ice cores from the Byrd Station in Antarctica where it was impossible to interpret successive summer and winter layers. The isotopic variation was too irregular to be acceptable for paleoclimatic use. Still, the hydrogen and oxygen isotope values have been used as record of climatic conditions in terms of calculated mean air temperatures, like for the Vostok ice core (Jouzel et al., 1987; Barnola et al., 1987).

For the Vostok ice core Jouzel et al. (1987) correlated the recent annual averages of the surface temperature with the recent snow hydrogen isotope ratio, using a correction model for the kinetic isotope effect. This relation was then used to calculate temperature deviations from the present surface temperature ($-55.5^{\circ}C$) for the whole 2083 m ice core covering 160,000 years. The authors must assume that the precipitation rate was constant throughout this long time span covering several glacial and interglacial stages. This assumption is highly questionable. Nor is it likely that the isotopic record has been unaffected by phase changes in the firn and brine-ice interactions in firn and ice (see Chapter 5) that alter the original light isotope ratios.

The attenuation and obliteration of the isotopic signature indicate that both firn and ice in the polar ice sheets do not stand up to the closed system criterion, absolutely essential for using this signature for paleoclimatic estimates. Distinct fluctuations of $\delta^{18}O$ on time scales of several years to many decades,

observed in many records, do not have necessarily climatic significance, and may be due to factors other than air temperature (Watanabe, 1978; Satow and Watanabe, 1987; Grootes, 1990).

7. LAG BETWEEN CO₂ LEVELS AND TEMPERATURE CHANGES

The slightly increasing mean temperature of the Northern Hemisphere surface air, which was observed from the start of this century to the 1930s, took place prior to the major "greenhouse gas" emissions (Michaels, 1990). In the Mauna Loa record of CO₂ atmospheric concentration (Keeling et al., 1989) the peak values lag behind the global continental temperature maxima by about five months (Kuo et al., 1990). Kuo et al. (1990) noted that changing temperatures lead to changes in the amount of CO₂ outgassing or dissolution in the ocean, and to variation in biological activity, and thus to CO₂ level changes in the atmosphere. The five month lag time of CO₂ changes behind temperature changes, indicates that the causality is: temperature–to–CO₂. If heat trapped by CO₂ was the cause, the opposite sequence of maxima should be observed. Barnett (1990) suggested that the interrelation between the two variables (i.e. CO₂ and temperature) may be due to temperature changes arising from natural climate variability, and has nothing to do with an increasing "greenhouse effect". Barnola et al. (1987) found that in the Vostok ice core, reportedly covering the past 160,000 years, "the CO₂ change [was] clearly lagging behind the δD decrease", δD being interpreted as a paleo–temperature indicator. However, as discussed in Jaworowski et al. (1992) both the CO₂ and stable isotope data from this core are affected by the processes in the ice sheet and artifacts in the highly contaminated ice core, and therefore do not represent the original paleo–composition of the atmosphere and of the precipitation.

Ocean water is a large sink for CO₂. Because of CO₂'s retrograde solubility in water, increased temperature causes degassing of CO₂ from the ocean to the atmosphere (Segalstad, 1990). This "thermal solubility pump" accounts for 70% of the CO₂ flux from the ocean to the atmosphere, while "the biologic pump" accounts for the remaining 30% (Volk and Liu, 1988). It has been estimated that 4000 GT of CO₂ (equivalent to 1000 GT of carbon) is fluxed from the ocean *via* the atmosphere to the continental biosphere during the transition from a glacial to an interglacial stage (Faure, 1990), owing to these two "CO₂ pumps" only. Other natural carbon fluxes (weathering, volcanism, hot springs, carbonate sedimentation, degassing by metamorphosis of rocks, etc.) are not included in this figure.

8. GLOBAL TEMPERATURE RECORDS

As indicated before, it was assumed that since the middle of the 19th century the concentration of CO₂ in the atmosphere has increased by about 25% (IPCC, 1990). According to the General Circulation Models (GCMs) this should have increased the global mean air temperature by up to about 2.5°C today. These models have predicted the strongest warming, 8 to 10°C, to occur in the Arctic. The surface temperature measurements do not confirm these predictions. Stratospheric temperatures, which according to climatic models should decrease in a "greenhouse-gas" enriched atmosphere, did not show a statistically significant decline since 1960 (Angell, 1986).

Attempts to find a warming trend signal in the long temperature records are, to a large extent, based on inspection of smoothed curves ("running means") and not on more reliable time series analyses. The way in which smoothing procedures may totally change the statistical properties of the original time series, and lead to unrealistic conclusions, has been treated by several authors (see e.g. Hisdal, 1956). Variations with long periods are emphasized in a fascinating manner, and short period "noise" is suppressed, the final result depending on the type of smoothing filter applied. Even completely random series may, on the basis of visual inspection, show convincing "climatic changes" after having been beautified by such linear operations (cf. Haavelmo, 1951).

Hansen and Lebedeff (1987, 1988) found that the average global land temperature increased about 0.7°C during the past one hundred years. Other studies suggested that the global land and sea-surface temperatures rose by about 0.5°C (see review in Monastersky, 1989). Hansen (1988) stated in front of the U.S. House of Representatives that he had "99% confidence" in the reality of the global warming trend, and in the cause/effect relationship between a 0.7°C global warming and anthropogenerated "greenhouse" alterations. This statement was criticized on theoretical grounds (see e.g. review in Kerr, 1989) and it was also found that the uncertainty of the estimated past global temperatures is about the size of the warming signal (Barnett, 1989 – after Monastersky, 1989). The corrections applied on the global data set are of the same magnitude or larger than the warming trend they are claimed to show, and the results seem very doubtful (Frydendahl, 1989).

A recent study of the NASA climate records in the United States showed a warming of 0.4°C in the twentieth century. However, this temperature increase could be influenced by an urbanization effect on measurements taken at meteorological stations situated in or near the cities (Karl and Jones, 1989). Also, it was pointed out that a notable part of the increase was due to an error of the computer program when NASA supplied data to NOAA for analysis (Karl – after Michaels, 1990).

Hanson et al. (1989) found that the records from the 48 contiguous United States do not indicate any statistically significant evidence of an overall increase in annual temperatures or change in annual precipitation between 1895 and 1987.

A new study of the worldwide ocean temperatures since 1850, carried out by a group from MIT shows little or no global warming over the past century (Newell et al., 1989). The authors found that the average

ocean surface temperature is now virtually the same as it was in the 1940s. As two thirds of the buildup of CO₂ have taken place since 1940, the MIT data do not support the General Circulation Model calculation results.

Reynolds et al. (1989), analyzing surface and satellite measurements, concluded that there is no evidence of any warming trend in the ocean surface water between January 1982 and June 1988. This finding refuted an earlier claim by Strong (1989) that the sea surface temperatures increased in this period by as much as 0.1°C per year.

The variability of natural climatic fluctuations, and human influence on temperatures (urban and "heat island" effects) make it difficult to obtain homogeneous time series of annual global temperatures (Landsberg, 1974; Groveman & Landsberg, 1979). The temperature variations over continents are, on the average, 4–6 times larger than over oceans during the winter, and 2–3 times larger on a yearly basis. The area ratio continents/oceans between 15 and 70° North is 0.88, but only 0.14 between 0 and 70° South. For an area weighed arithmetic mean calculated for the Northern and Southern Hemisphere, the temperatures measured over continents will therefore dominate the Northern Hemisphere mean. A major problem lies in making the weighed global annual mean temperatures representative when more temperature data are available over continents than over oceans. This problem has still not been satisfactorily solved.

Long, relatively reliable series exist for the Northern Hemisphere from Europe, North America, Soviet Union, and Japan. These data were used by Borzenkova et al., (1976) and by Groveman and Landsberg (1979) for calculating weighed annual average temperatures for the Northern Hemisphere (Figure 9). In order to extend the time series back in time (between 300 – 400 years B.P.) Groveman and Landsberg used records of tree ring thickness from Finland and Alaska, which had correlated well with later instrumental temperature records. The older part of their time series is the least reliable one.

A spectral analysis of the about 400 years long time series reveals that almost half of the variance can be explained by a periodic variation with a wavelength of 99 years (Groveman and Landsberg, 1979). A plausible explanation of this periodic variation is cataclysmic volcanic eruptions occurring at about this time interval, e.g. Laki (Iceland) 1783–1785 and Krakatau (Indonesia) 1883. These eruptions released sulfur dioxide explosively to the stratosphere, where the SO₂ combined with water to sulfuric acid, effectively blocking a part of the incoming solar radiation (Segalstad, 1983; Palais and Sigurdsson, 1989). It has been calculated from geologic evidence that Laki's 1783 eruption caused the formation of some 90 million tons of sulfuric acid in the stratosphere, while the 1883 Krakatau eruption contributed some 30 million tons. Other volcanic eruptions also contribute steadily to the atmospheric input of sulfur. For example, the small 1981 eruption of the Krafla volcano (Iceland) contributed to the formation of some 100,000 tons of sulfuric acid (Palais and Sigurdsson, 1989).

The irregular influence of volcanoes on the Earth's climate, makes it necessary to look at time series which are several times longer than the intervals between the eruptions and longer than about 100 years. For a discussion on time spans and resolution of various climatic records see e.g. Webb (1985).

It is interesting to compare the nearly 400 years long series with a shorter portion from the years 1850–1975. Both data sets show nearly the same arithmetic means and standard deviations (both normally distributed). Adapting a linear trend to the data, the long time series shows almost no change at all ($+0.076^{\circ}\text{C}$ per 100 years), while the short series (1850 – 1975) gives a small increase ($+0.33^{\circ}\text{C}$ per 100 years). It is important to note, however, that the calculated trends "explain" only about 15% of the variances in the data sets.

A careful statistical analysis of the long-term series of temperature (1869–1985) from widely distributed European stations did not demonstrate convincingly that there has been a CO_2 effect upon the European climate so far (Coops, 1991).

The rescaled range methods of Mandelbrot and Wallis (1968, 1969 a, 1969 b) are appropriate for examination of certain long geophysical records. They were used, for example, for studying the many thousand year long record of water level, flooding and drought of the river Nile. Such records have in most cases been found to be "fractal noise", and statistics based on random series cannot be used. This method tests the persistence tendency of the data (i.e. if high or low levels tend to occur over a long time). The method can also put constraints on the likelihood of getting extreme values in the future.

Using this procedure, Frøyland (1992) found for the 400 years long temperature series (Figure 9) a strong tendency for the temperature to remain within the same range for times much longer than what would be expected if there was statistical independence in the series. This means that there exists a strong persistence tendency in the series (a warm year is likely to be followed by another warm year, a warm decade is likely to be followed by another warm decade, etc.).

Based on examination of shorter (100–150 years) series many researchers have concluded that a recent rise in temperatures is caused by only one, anthropogenic, cause and projected this signal into the future to give 3.5 to 5.0°C higher annual global temperatures 60 years from now.

By inspection of the long time series (Fig. 7) we see three other similar temperature rises (starting at about 1835, 1675, 1605). If it is true that the anthropogenic influence by deforestation, agriculture and burning of fossil fuels started about 1750, we should be able to see this as a signal in the temperature data over the last 200 years, making these data noticeably different from those of the foregoing 200 years. This is not observed. Even a claimed recent rise in the 1980s (not shown in Figure 9) is less dramatic than the rise in temperatures from about 1810 to about 1830.

Using the temperature series compiled by Jones et al. (cf. Jones, 1988) for both hemispheres Demarée (1990) found by statistical tests that the warming occurring around 1920 in the Northern Hemisphere, and somewhat later in the Southern Hemisphere, had the character of a comparatively abrupt change of the mean temperature level. Such "climatic jumps" have been pointed out by several authors also for other periods and for other regions (see e.g. Yamamoto et al., 1987). It seems unrealistic to ascribe this phenomenon to a gradually increasing CO_2 concentration. It may be more plausibly explained on the basis of the non-deterministic theory of climatic change proposed by Lorenz (1976), without assuming any variation of external or boundary forcings for the climatic system.

We conclude that the nature of the temperature series is such that no signal of human-induced global warming is significantly traced in the best available temperature series for the Northern Hemisphere. This agrees with the results of investigation of the currently available data bases for the global land and sea surface temperatures carried out by Frydendahl (1989). He concluded that the uncorrected data indicate rather cooling than warming of the oceanic surface waters and of surface oceanic air during the last 100 years, and that there exists no unequivocal information which could prove that the warming of the globe occurred during the past 130 years. High recent temperatures are not significantly different from earlier similar excursions (Fig. 7), and are not of a magnitude or duration (part of a 200 year long increasing trend) that is unique or alarming compared to earlier temperature fluctuations. Recent high temperatures can be explained on the basis of the statistical properties of the series, according to dynamic systems theory (Frøyland, 1992).

The mean 3.3% annual rise in the release of CO₂ from burning of fossil fuels (Elliott et al., 1985) since about 1750 should give a statistically significant signal in the temperature, if the current models for the global carbon cycle and the "greenhouse effect" are correct. Such a signal is not observed. As stated before, the 400 years temperature record represents a series with a strong persistence tendency. This record (which includes more than 200 years of increased CO₂ emission from man-made sources) may be characterized as resembling "fractal noise". Its statistical analysis indicates that processes that were operating in this period are unlikely to produce 3.5 to 5.0°C global heating, regardless of their cause (Frøyland – private communication).

Analysis of the first 10 years (1979 to 1988) of satellite measurements of lower atmospheric temperature changes reveals no heating or cooling tendency for the 10-year period (Spencer and Christy, 1990).

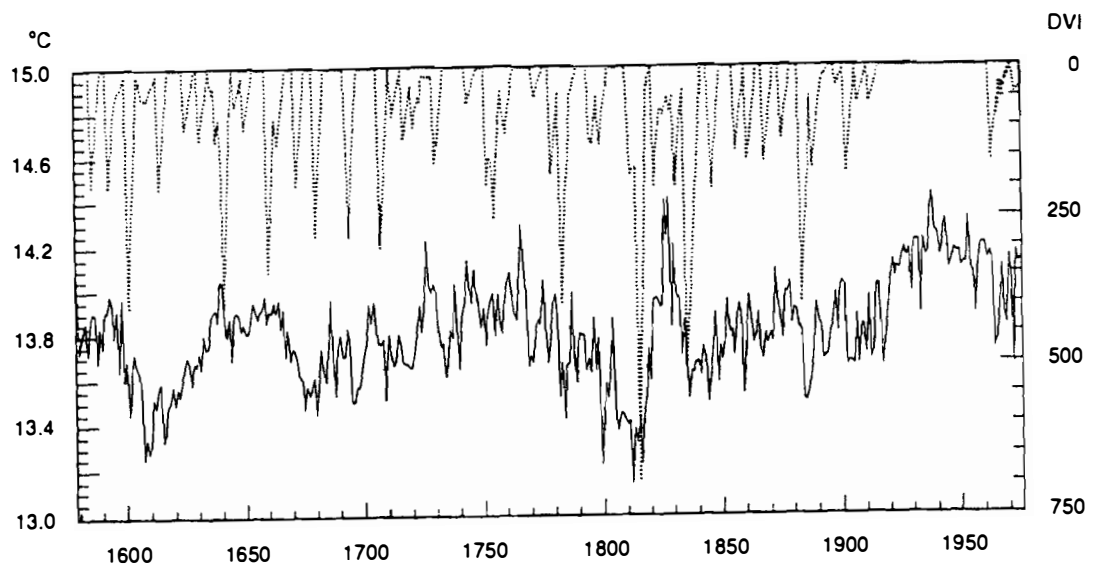


Figure 9. Lower curve: Northern Hemisphere annual temperatures (data from Borzenkova et al., 1976 and Groveman and Landsberg, 1979). Upper curve: Volcanic Dust Veil Index, D.V.I. (data from Lamb 1970, 1978), with increasing values downwards.

9. AIR TEMPERATURES AND GLACIERS AT HIGH LATITUDES

Because of the combined effect of the "greenhouse gases", we should, according to Michaels (1990), have effectively gone more than half way to a doubling of CO₂. According to General Circulation Models the strongest greenhouse warming should be expected in high latitudes (in the Arctic about 2°C in summer and 8–14°C in winter with CO₂ doubling), causing a decrease in the mass of polar ice, and rise in sea level with catastrophic consequences. Observations, however, do not support these predictions.

Temperature series from the Scandinavian peninsula, Denmark and Greenland for the last 120–130 years give no evidence for a positive trend during this period (Aune, 1989; Frydendahl, 1989). These records show that in this region in our century there was a general increasing temperature tendency up to the 1940s, followed by a slight decrease towards the end of the series. Long-term temperature records in Svalbard started in 1912 at Green Harbour. During the first years the smoothed mean temperature rose considerably until the 1920s, particularly during the winter season (Birkeland, 1930; Hesselberg and Birkeland, 1940). Since then there have been several "nice" waves in the Svalbard temperature series (Figure 10), as in all smoothed series, but no definite sign of an increasing "greenhouse" warming, that would justify a statistical analysis (Hanssen–Bauer et al., 1990).

Five studies of other Arctic temperature records presented by Michaels (1990) show similar variations as those found in the Norwegian Arctic. On Semlya Frantsa Iosifa a decrease of average annual temperature of more than 4°C was observed between 1950 and 1965 (Frydendahl, 1989), in agreement with the trend recorded in Svalbard.

There is no simple link between glacier mass balance and air temperature. In many regions an increase of glaciers is connected with mild winters and increased precipitation, and with cool summers. This is opposite to the popular concept on the relationship between glaciers and temperature. Nevertheless glacier variations are an important issue in the current discussion on the "greenhouse" warming and sea level changes.

Lefauconnier and Hagen (1990) and Hagen and Liestøi (1990) found that the glaciers Brøggerbreen and Lovenbreen in Svalbard showed recent deceleration of loss of ice mass. This is in agreement with the study of Koerner et al. (1989) who have determined the ice mass balance for the past 10 to 30 years at four ice caps in the Canadian Arctic, and found no indication of increasing ablation. In the Canadian ice cap Koerner et al. (1989) found that the conditions during the last years constitute a marked contrast to the heavy melting years that characterized the warm period from the 1960s to the early 1980s. During the second half of the 1980s, there was an increase in the ice mass at the Melville South and Meighen ice caps. Since about 1968, the advance of small glaciers in West Greenland coincided with a period of decreasing summer temperatures, and could be seen as a direct response to this climatic deterioration. Six out of the nine glaciers studied continued to advance at least until 1978 (Gordon, 1980). After 1976 a change from negative into positive mass balance was observed at Wolverine Glacier in Alaska (Mayo and March, 1990). In the Swiss Alps about ten times more glaciers were advancing in the 1980s than around 1900 (Lamb, 1988). Also individual Himalayan glaciers appear to be advancing (Benxing et al., 1984).

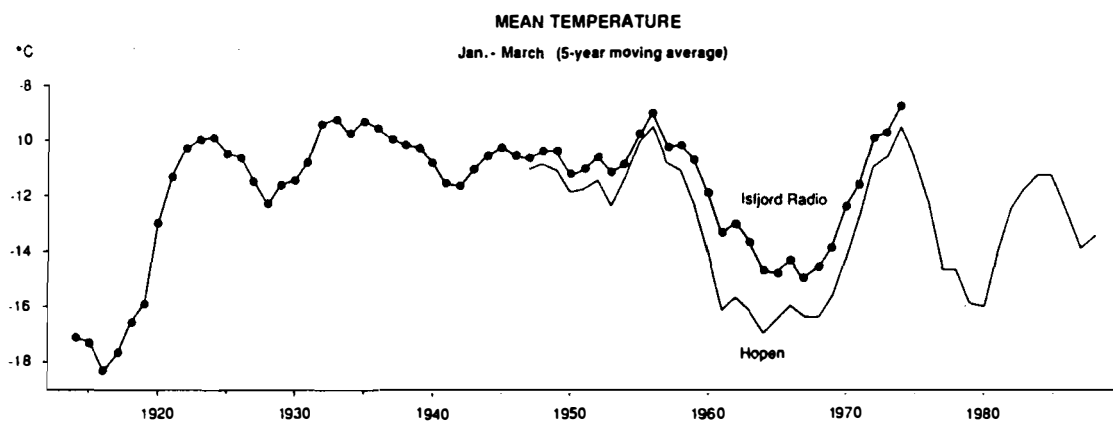


Figure 10. Five-year moving average temperature for January–March for the stations Isfjord Radio (78°04'N, 13°38'E) and Hopen (76°30'N, 25°04'E).

The new satellite surveys indicate that both the ice caps of Greenland and Antarctica are now increasing, corresponding to a sea level lowering of 0.45 and 0.75 mm per year, respectively (Meier, 1990). At about 1950 the greater part of the Inland Ice margin in South and West Greenland was receding and thinning. By about 1985 many previously receding parts of the inland ice margin were in a state of advance. At present the zone of advance is spreading from the highland to the lowland regions (Weidick, 1991, and references therein). Independent evidence for recent advance and thickening of the Inland Ice in Greenland comes from geodetic (Seckel, 1977) and from satellite altimetry (Zwally, 1989).

Zwally (1990) and Zwally et al. (1989) found that the southern 40% of the Greenland ice sheet was increasing vertically by about 23 cm per year between 1978 and 1986. This indicates a 25 to 45% excess in ice accumulation over the amount required to balance the outward ice flow. The corresponding sea-level decrease is 0.2 to 0.4 mm per year. An increase in snow accumulation in Antarctica, corresponding to a sea level lowering of 1.0 to 1.2 mm per year was also reported by Morgan et al. (1991). Hence the thermal expansion of the sea water during a warming period can thus be counterbalanced. Of course, during cooling periods the water of the oceans will tend to show thermal contraction.

The above discussion supports the opinion (Wigley et al., 1989) that the anthropogenic increasing "greenhouse" warming signal has not yet been detected in a rigorous way.

10. CONCLUDING REMARKS

- ★ As indicated by the measurements of radiocarbon (^{14}C) from nuclear test explosions the residence time of CO_2 in the atmosphere is only 5 years. Assigning a longer atmospheric residence time (up to 200 years) for man-made CO_2 was made to fit the pre-conceived idea that the 19th century CO_2 atmospheric level was 25% lower than now. The value of about 280 ppmv, widely accepted from glacier studies as the pre-industrial atmospheric CO_2 level results from invalid assumptions, processes in ice sheets and artifacts in ice cores.
- ★ The atmospheric CO_2 is constantly changing and adjusting its concentration according to the natural changes in the Earth's temperature. These changes are governed by inorganic thermodynamic gaseous, aqueous and mineral equilibria, and by biologic processes. Anthropogenic CO_2 is negligibly small compared to the gigantic natural reservoirs and fluxes of natural CO_2 .
- ★ CO_2 has a high solubility in water. Lower aqueous solubility of CO_2 at higher temperature cause the oceans to degas CO_2 to the atmosphere when the sea and air temperature rises as a result of natural climate change. This leads to an increase of CO_2 concentration in the atmosphere, which in this case is an effect and not a cause of climatic change. The atmospheric CO_2 increases in the 20th century were found to lag behind increases of the surface air temperature. A warming effect of the increased atmospheric CO_2 may be counterbalanced by powerful negative feedback mechanisms, such as increased cloudiness.
- ★ Radiocarbon (^{14}C) studies show that the upper ocean turn over the dissolved atmospheric CO_2 in a short time (a few decades), thus effectively eliminating the bulk of the man-made CO_2 .
- ★ The exploitable total fossil fuel carbon reservoir is only 11 times larger than the atmospheric carbon reservoir. About fifty parts of CO_2 are dissolved in the oceans for each part released to the atmosphere. Therefore, a permanent doubling of the atmospheric CO_2 cannot be realized from burning of fossil fuels only, all other things being held constant.
- ★ There are several methodological uncertainties in the analysis and data processing of the current atmospheric CO_2 concentration. Further investigations of these problems seem necessary.

- ★ The estimate of "pre-industrial" atmospheric CO₂ concentration cannot be based on studying gas inclusions in ice cores, or carbon isotopes in tree rings, using the current analytical techniques. The sampling and analytical methods used give results that have an uncertainty larger than the claimed variations.
- ★ The presence of liquid water in glacier ice at low temperatures, and the physical and chemical processes involved are likely to make ice core results unrepresentative of the original chemical and isotopic composition of the ancient atmosphere.
- ★ Temperature estimates from hydrogen and oxygen isotopes in glacier ice are highly uncertain, and in most cases meaningless because ice-brine interactions took place in the glacier ice, and because of partial transitions between solid, liquid, and gas states of H₂O, taking place in the ice sheets and in the ice cores.
- ★ Clear indications of atmospheric heating caused by anthropogenic releases of CO₂ or other "greenhouse" gases have not been found in the temperature records.
- ★ For several arctic and temperate glaciers a reduction of the negative mass balance was found. Both in Greenland and Antarctica an increase of ice mass was recently observed, which indicates that an imminent rise in sea level is not likely. A claimed thermal expansion of sea water during the last warming period may thus be counterbalanced.

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12. SAMMENDRAG (NORWEGIAN SUMMARY)

Forutsigelsene om en menneske-skapt (antropogen) klimaendring gjennom brenning av fossile karbon-brennstoffer (kull, gass, olje) til CO₂-gass, er hovedsakelig basert på fortolkninger av målte konsentrasjoner av CO₂ i atmosfæren og i bre-is.

Viktig for Jordens CO₂-syklus er havet og mineralenes kjemiske likevekter. På grunn av deres enorme buffer-kapasitet, stabiliserer de den geokjemiske likevekt for CO₂-gass mellom hydro-, atmo-, litho- og biosfæren. Nyere studier av radiokarbon (¹⁴C) viser at sirkulasjonstiden for oppløst organisk karbon i de øverste lag i havet bare er noen få tiår. Dette betyr at CO₂ dannet ved brenning av hele Jordens forråd av fossile karbon-brennstoffer vil bli oppløst i havet før atmosfærens konsentrasjon av CO₂ kan dobles i forhold til det nåværende nivå.

Målinger av CO₂ i atmosfæren i det nittende århundre ble foretatt med en unøyaktighet på opptil 100%. En verdi på 290 ppm (volumdeler av en million) ble valgt som en gjennomsnittsverdi for det nittende århundre, ved å forkaste "ikke-representative" verdier, som var 10% eller mer forskjellige fra "det generelle gjennomsnitt for denne tiden". En avgjørende subjektiv faktor inngår derfor i anslaget for det før-industrielle nivå for CO₂ i atmosfæren.

Mauna Loa-observatoriet på Hawaii har vært regnet som et ideelt sted for måling av det globale CO₂-nivå. Imidlertid er observatoriet lagt til toppen av en aktiv vulkan, som gjennomsnittlig har ett utbrudd hvert 3,5 år. Det er uavbrutt utstrømming av CO₂ fra en sprekkesone bare 4 km fra observatoriet, og verdens største aktive vulkankrater ligger bare 27 km fra observatoriet. Disse spesielle forhold gjorde det nødvendig å innføre "redigering" av målingene som fast prosedyre. CO₂-verdiene har derfor vært gjenstand for en viss skjønnsmessig vurdering før publisering. Lignende prosedyrer blir også brukt ved andre CO₂-observatorier. Den teknikk, som brukes for måling av atmosfærisk CO₂, kan gi ikke-representative resultater for CO₂-konsentrasjonen.

CO₂-konsentrasjonene i luftbobler innesluttet i bre-is blir ofte tatt som representative for tidligere atmosfæriske konsentrasjoner. Det ble antatt at sammensetningen av luften i boblene forble uendret. Dette var igjen basert på den antagelse at det ikke kunne være væske i isen ved en gjennomsnittlig årstemperatur på rundt -25°C, og at det derfor ikke kunne ventes noen forandringer som skyldtes diffusjon. Imidlertid ble det nylig funnet årer fylt med væske i isen i Antarktika ved temperaturer helt ned til -73°C. Tallrike studier viser at flere kjemiske og fysiske prosesser kan gjøre at CO₂-innholdet i isen enten øker eller avtar kraftig i forhold til innholdet i den opprinnelige atmosfære. Ved flere undersøkelser ble det funnet at CO₂-nivået i før-industriell is var det doble av nivået i dagens atmosfære.

Metoder som benytter tørr ekstraksjon av CO₂ fra knust is, frigjør bare omtrent halvparten av denne gassen fra isen. CO₂ i luftboblene kan trenge gjennom isen ved diffusjon eller oppløsning i væske som er til stede langs korn grensene, med en hastighet forskjellig fra luftens andre gasser. Dannelse av faste CO₂ klatrater (hydrater) er et problem for bestemmelsen av CO₂-mengden i gassinneslutninger i is. Andre gasser danner også klatrater, men ved andre temperaturer og trykk. Dette kan lede til betydelige forandringer i gass-sammensetningen i inneslutninger ved forskjellige dyp. Derfor er CO₂-målinger av luftbobler innesluttet i is ikke representative for den opprinnelige atmosfære. Dette innebærer at bre-is ikke

kan betraktes som et bestandig materiale. Iskjerner vil derfor ikke være et tilfredsstillende materiale for observasjon av atmosfærens utvikling gjennom lange tidsrom.

Det kan også være vanskelig å fastsette alderen til luftbobler innfanget i is. Dette medfører nok en usikkerhet i måleresultatene, til og med fra de øvre ~100 m is avsatt på Grønland og i Antarktika. Det opprinnelige $N_2/O_2/Ar$ -forhold i luften er ikke bevart. Forholdene er mer lik de man finner for oppløselighet av gasser i vann. Gassblærene må i hovedsak ha blitt dannet ved utskillelse da vannet frøs, og ikke fra gjenslukkede kanaler, som opprinnelig var åpne til luften.

Beregninger av tidligere tiders temperaturer basert på lette stabile isotoper (D/H og $^{18}O/^{16}O$) i is er også beheftet med stor usikkerhet. Etter oppdagelsen av væske mellom iskrystaller i dypfrosset is i Antarktika vil faseforandringer måtte ventes. Det kan regnes med stor isotop-utbytting og stor forandring i isotop-forholdene, noe som medfører at beregnede paleo-temperaturer fra isotop-forholdene vil være meningsløse når faseforandringer oppstår i nærvær av en mobil væskefase.

Det har vært gjort forsøk på å beregne den tidligere konsentrasjon av CO_2 i atmosfæren fra stabil-isotopforholdet for karbon ($^{13}C/^{12}C$) i træs årringer. Det konkluderes her med at CO_2 -innholdet i atmosfæren beregnet fra slike analyser ikke kan bli brukt som en gangbar metode i paleoklimatologi, og ikke som bevis for forandring i atmosfærens CO_2 -innhold.

Det mest omtalte "drivhuseffekt-signalet", en antropogen økning av den globale lufttemperatur, påstått å ha funnet sted gjennom de siste tiår, er ikke blitt bekreftet gjennom studier av lange temperatur-serier.

Det har vært hevdet, i henhold til modellberegninger, at denne oppvarmingen skulle være mest merkbar i Arktis. Imidlertid er det ikke påvist noen temperaturøkning i dette området i løpet av de siste to tiår. Over flere større områder i Arktis og Antarktis viser breene positiv eller avtagende negativ massebalanse. Dette tyder ikke på at den påståtte økning av havnivået er særlig sannsynlig.

